





**D.N. TRIFONOV**

**THE RARE-EARTH  
ELEMENTS**

## CONTENTS

English Editor's Foreword	vii
Russian Editor's Foreword	viii
Author's Preface	ix
Introduction	xiii
Chapter I. History of the discovery of rare-earth elements	1
1. A mineral from Ytterby	2
2. Modern times—new “earths”	4
3. The “submerged rock” of the periodic system	7
4. The elusive Element 61	16
5. The role of Russian scientists in the study of the rare-earth elements	24
Chapter II. Why is the family of rare-earth elements peculiar?	25
1. The periodic system and the structure of electronic shells	25
2. The properties of the rare-earth elements in the light of their electronic structure	35
3. A brief account of the geochemistry of the rare-earth elements	43
Chapter III. The properties of the rare-earth elements and methods for their separation	52
1. The physical and chemical properties of the rare-earth elements	52
2. From the mineral to the pure metals	62
Chapter IV. Practical applications of the rare-earth elements	73

Chapter V. The present state of the problem of the rare-earth elements	93
1. Once more on the position of the rare-earth elements in the periodic system	93
2. Lanthanides and actinides	96
3. Nuclear chemistry of the rare-earth elements	101
4. Another periodic system	107
5. Does promethium exist in nature ?	109
6. The origin of the elements	111
Conclusion	115
Notes	119
Suggested Further Reading	125
Index	127

## ENGLISH EDITOR'S FOREWORD

IN editing the English edition of this book I have taken great care to alter as little of the subject matter as possible. In a number of cases, however, where I have felt it necessary to question a statement of the author's or to elucidate a particular point, I have added footnotes. It must be emphasized that the views expressed in them represent my opinion only and possibly not that of the author.

It should be noted that by definition Dr. Trifonov excludes scandium and yttrium from the rare-earth groups, a classification with which I myself would disagree.

This book will serve as a useful introduction to the study of the rare earths, that highly intriguing group of elements whose chemistry has occupied much of my time during the past 20 years and which are now beginning to be applied widely in industry. I feel that students, professional scientists and all interested in the subject will find much of value in this volume, especially as a reflection of the ideas of workers in the Soviet Union.

R. C. VICKERY  
Malibu, California.

## RUSSIAN EDITOR'S FOREWORD

CERTAIN elements and their compounds, previously considered rare and of no practical interest, are being introduced on a large scale in industry to meet the growing demands of the modern world.

The family of rare-earth elements (lanthanides), which includes approximately one-fifth of all the metals occurring on the earth, is of very great interest for several reasons. The peculiar physical and chemical properties of the lanthanides and their compounds, and their relatively high abundance on the earth's crust, have engaged the attention not only of individuals taking an interest in science but also of entire scientific bodies. Unfortunately, however, the scale on which these elements are used in Soviet industry is far from adequate. This is so, although the Soviet Union possesses very rich deposits of rare-earth ores and all that is necessary for their extensive application in industry and, in particular, in metallurgy.

The author, a research worker at the Institute of the History of Science and Technology of the Academy of Sciences, U.S.S.R. has given an account, which is both lively and easily intelligible, of the long and extremely involved history of the discovery of these elements, their properties, the methods for their separation, the present state of the problem and some prospects of future developments in this branch of chemistry.

Although the book is primarily intended for laymen, specialists also are likely to find some interesting facts in it. It is to be hoped that the engaging story told here will not only succeed in creating an interest for this field among people with little knowledge of it but also help those concerned with bordering domains of science and technology to form a clearer conception of the immense potentialities inherent in the extensive use of these elements, which possess such unique properties.

## AUTHOR'S PREFACE

AMONG the 102 elements known to men, there are 15 whose properties resemble each other like two drops of water.

These are the so-called rare-earth elements. They are situated at the centre of Mendeleev's table.

Their name originates from the Latin *terra rara*, which means "rare earth".

For a long time they were considered really rare. Only the investigations of the last two decades have shown that they are far more abundant on the earth's surface than metals like lead, mercury and gold, which have long been known to men.

Prospects of their application to practice were once considered poor; their main application being in the preparation of flints for automatic cigarette lighters, etc. But now the rare-earth elements constitute some of the most important materials of modern technology. Their application ranges from space rockets to medicinal preparations.

Their confused history is full of contradictions and riddles and is complicated to an extent not to be found in the entire history of inorganic chemistry. Even the great Mendeleev, the propounder of the periodic law, could not solve the main riddle of the rare-earth elements—the problem of their position in the periodic system.

Their history has covered a path extending from the discovery of "yttria" by the Finnish chemist Johann Gadolin to the artificial production of promethium, an element not yet found on the earth's surface.

Rare-earth elements previously used to attract the attention of a few specialists only. Now, people belonging to the most varied professions are interested in them.

Unfortunately the number of review articles and books on rare-earth elements in Russian is very small\*. Among the popular books on the subject, we wish to mention G. Hevesy's

\*Many are, however, available in the English language, see footnote on page x.



valuable book *Rare-earths from the point of view of atomic structure*, which was published in Russian 30 years ago but is of interest even to-day.

The author wishes to express his deep gratitude to Yurii Sergeyevich Sklyarenko for his valuable suggestions and friendly advice during the editing and final preparation of the manuscript. Dr. Sklyarenko has added a few remarks which will enable the reader to gain a better understanding of the problems considered in the book.

Yost, Russell and Garner: *The Rare Earth Elements and their Compounds*, Wiley, 1947.

Vickery: *Chemistry of the Lanthanons*, Butterworth, 1953.

Vickery: *Chemistry of Yttrium and Scandium*, Pergamon, 1960.

Vickery: *Analytical Chemistry of Rare Earths*, Pergamon, 1961.

Love: WADC Report 57-666 Astia Document No. 155685, June 1958.

Gschneider: *Alloy Systems of the Rare Earths*, Van Nostrand, 1961.

## PREFATORY NOTE

THIS book gives an account of one of the most interesting problems of present-day inorganic chemistry—that of the rare-earth elements (lanthanides). These elements, previously considered unpromising for practical purposes, are now finding application in the most varied fields of science and industry. The book describes the properties of the rare-earth elements, the methods of separating them and obtaining the pure metals, and relates the extremely involved history of their discovery. The last section of the book is devoted to the subject of the present state of the problem of the rare-earth elements.

## INTRODUCTION

“RARE-EARTH elements are a forgotten branch of chemistry”, many scientists used to assert a few decades ago. If at that time such a judgement had any foundation, it can now sound only ironical because the rare-earth elements now form one of the leading branches of inorganic chemistry. Having become so through the great achievements of science and technology in the last few years.

The development of technology, and chiefly nuclear technology, required new materials with the most varied properties. It is natural that scientists and engineers should have turned their attention to rare-earth elements also.

The achievements of nuclear physics made it possible to produce, artificially, several new transuranic elements and helped to strengthen the so-called actinide hypothesis<sup>(1)</sup>. The study of their properties required thorough investigations in the field of the chemistry of rare-earth elements or lanthanides. The lanthanides and actinides were found to have so many properties in common that a detailed study of the latter would have been impossible without a deep knowledge of the chemistry of the family of rare-earth elements.

And finally, the advances in nuclear chemistry, the discovery of nuclear reactions occurring in nature—on the earth’s surface and in outer space—brought the solution of the problem of the origin of chemical elements, one of the greatest problems of natural science hitherto unsolved, to the forefront. The family of rare-earth elements, because of its exceptionally peculiar nature, should play no insignificant role in clearing up this mystery.

Hardly any of the great minds, even of the comparatively recent past, could imagine the importance the family of rare-earth elements would acquire in our time. This is the story which will form the subject of this book. For the present we will remind the reader what these elements are.

The name is given to 15 chemical elements with the serial

numbers 57–71. Arranging them in the ascending order of their nuclear charge, we get the following series:

Z	Element	Symbol	Z	Element	Symbol
57	Lanthanum	La	65	Terbium	Tb
58	Cerium	Ce	66	Dysprosium	Dy
59	Praseodymium	Pr	67	Holmium	Ho
60	Neodymium	Nd	68	Erbium	Er
61	Promethium	Pm	69	Thulium	Tm
62	Samarium	Sm	70	Ytterbium	Yb
63	Europium	Eu	71	Lutetium	Lu
64	Gadolinium	Gd			

In Mendeleev's periodic table the elements from  $Z = 57$ –71 are usually arranged in a box, as shown in Fig. 1.

The reason for such an arrangement lies, as we shall see later, in the peculiarity of their electronic structure and, as a consequence, in the extraordinarily close similarity of their properties. All these elements are typical metals; characteristically they appear together in ores and minerals. Yttrium ( $Z = 39$ ), which closely resembles them in its properties, is usually included with them, although it is not a member of the rare-earth family as it is understood to-day. This is because in the historical development of the chemistry of rare-earth elements it was very closely associated with them and initiated the yttrium group of these elements. Scandium ( $Z = 21$ ), possessing similar properties, is also sometimes included with them.\*

The reader has probably noted already that we have used two terms to denote the family of elements with  $Z = 57$ –71: rare-earth elements and lanthanides. We would point out that the first definition is wider since it includes lanthanum. The name lanthanoid denotes “lanthanum-like” and embraces elements from cerium Ce ( $Z = 58$ ) to lutetium Lu ( $Z = 71$ ), but chemists often use it implying lanthanum also.

The terms “lanthanides” and “rare earths” are also found in scientific literature. The first of these signifies the same concept as lanthanoids. As regards the second, it prevailed for at least

\*This classification is slightly different from the accepted practice of calling the elements, La through Lu the “lanthanons” or “lanthanides” and considering the “rare earth group” to be the lanthanons plus yttrium and scandium.

130 years out of the 165-year old history of the rare-earth elements. Now this name sounds archaic, since the old concept of "earth" has disappeared from the usage of chemists. As regards "rarity", they are by no means rare elements, as the latest geochemical investigations show.

We shall use the term "rare earths" only when speaking of the history of the discovery of rare-earth elements. The first chapter of the book is devoted to this subject.

In the second chapter the reader will learn about the electronic structure of the rare-earth elements and the effect of the peculiarity of this structure on their properties.

The third chapter gives a detailed account of the chemical and physical properties of the rare earths and their compounds, the methods of separating them and producing them in the metallic state.

The fourth chapter is devoted to the practical application of rare-earth elements.

The present state of the problem of rare-earth elements is briefly discussed in the fifth chapter.

Certain prospects of the possible application of rare-earth elements are mentioned in conclusion.

## CHAPTER 1

# HISTORY OF THE DISCOVERY OF RARE-EARTH ELEMENTS

IN the history of inorganic chemistry, if not in that of chemistry as a whole, it is difficult to find an area more confused and complex than the history of the discovery of the rare-earth elements. Perhaps the most complicated problem which Mendeleev's periodic table could not solve for a long time was that of the location of these elements. About half a century passed between the discovery of the periodic law and the final determination of the number of rare-earth elements and their position in Mendeleev's table.

Three examples, than which none could be clearer, bring out the whole complexity of the study of the chemistry of the rare-earth elements.

In 1839 the Swedish chemist Mosander discovered "didymium"—then thought to be a new chemical element. And it was only 46 years later that Auer von Welsbach, an Austrian, was to establish that didymium is actually a mixture of two elements: neodymium and praseodymium.

Element number 61 could not be discovered on the earth's surface, in spite of the numerous attempts of several scientists of different countries. Only progress in nuclear physics enabled the artificial production of this element.

The history of chemistry knows quite a few cases of erroneous discovery of chemical elements. If statistics are taken it will be found that the overwhelming majority of these belong to the domain of rare-earth elements.

And what about the doubts regarding the valency of the rare-earth elements, the absence of sufficiently accurate and reliable methods of isolating the rare earths and separating the individual elements, of methods of identifying the individual elements in a mixture? And the fact that obtaining the pure metals from the oxides was no easy task and chemists had to deal at

first with surprisingly similar oxides of the rare-earth elements? We believe the reader has realized the nature of the obstacles in the way of the scientists who set themselves the task of unravelling the tangle of the multitude of intricate problems.

The names of the investigators of the rare-earth elements, devoted selfless workers who carried out a painstaking and incredibly complicated task day after day, trying to arrive at the truth and solve, finally, the problem of the number of rare-earth elements, the reason for the similarity of their properties and for their position in the periodic table, must always remain in our minds. Although the last word on the solution of these problems belonged to physics, as we shall see later, it was through the work of Mosander and Delafontaine, Marignac and Saure, Boisbaudran and Cleve, Brauner and Urbain, Orlov and Welsbach, that an enormous amount of data was collected which in many ways determined the successes of the present-day development of the chemistry of rare-earth elements.

### **1. A Mineral from Ytterby**

The beginning of this history of rare-earth elements is associated with the small Swedish town of Ytterby, not far from Stockholm.

In the summer of 1788, Karl Arrhenius, a lieutenant in the Swedish army who devoted his leisure to researches in chemistry and mineralogy and the collection of minerals, discovered in an old open pit near Ytterby, an unknown black mineral reminding one of asphalt or coal by its appearance. Because of its high specific weight it was supposed that the mineral contained wolfram.

Seven years later, a specimen of ytterbite, as the new mineral was called, fell into the hands of the talented Finnish chemist Johann Gadolin, who subjected it to analysis. The scientist established that, in addition to the oxides of beryllium, silicon and iron, ytterbite contains about 38 per cent of the oxide of an unknown element, a "new earth", to which Gadolin gave the name "ytterbia"\*. Now let us take a look at the chemistry of a

\*(This was subsequently changed to "yttria" by Ekeberg).

more distant past and find out what chemists meant by the term "earth".

This concept included all substances which possessed the properties of alkalies, did not float and did not change on heating, were almost insoluble in water and evolved gas bubbles during reaction with alkalies. Such elements were long (almost up to the beginning of the 19th century) considered as "earths". The term "earth" included substances such as lime, barite, magnesia etc.<sup>(2)</sup> known from ancient times.

The investigation of the properties of the new "earth" carried out by Gadolin and confirmation of the data obtained by him by the Swedish chemist Ekeberg made it possible to establish that, although the new substance reminded one of the properties of the oxides of beryllium and calcium, it nevertheless differed from them by a number of features. Doubts regarding the individuality of "yttria" were dispelled. The list of elements was supplemented by one more member.

The mineral ytterbite was subsequently renamed gadolinite—thus emphasizing the work of the Finnish scientist. Gadolinite proved to be the beginning of a long chain of genuine and false discoveries, errors and achievements, successes and failures. It was not without purpose that the Finnish mineralogist Flink wrote that gadolinite "perhaps played a greater role in the history of inorganic chemistry than any other mineral."

The discovery of "yttria" aroused the interest of many scientists, in particular that of the Swedish scientist Berzelius and the French chemists Vauquelin and Klaproth.

Then again in 1803 Berzelius and Hisinger, and independently of them, Klaproth, discovered a new "earth" in the mineral ochroite (or cerite). Detailed investigations showed the very great similarity of its properties with those of "yttria". It was called "ceria" in honour of the small planet Ceres discovered at that time.

All the same, a very limited circle of chemists worked on the investigation of the properties of the new "earths". This is explained by the fact that extremely few deposits of the raw minerals were known and these were mainly concentrated in Scandinavia. It was no accident therefore that the new "earths"



began to be called “rare”—a term which was destined to remain fixed in chemistry for a long time.

The chemistry of the “rare earths” was still in its initial stages when the remarkable properties of Ceria—the significance of which became clear subsequently—were discovered. Vauquelin played a great role in discovering these properties. It is worthwhile dealing in some detail with the work of this French chemist—brilliant researches which would do credit to any later investigator.

At the request of Berzelius, Vauquelin analysed a sample of cerite in order to “determine whether the substance (ceria) should be classified with the earths or the metals”. The scientist investigated the new “earth” in all its aspects and drew the splendid inference that ceria has two degrees of oxidation. “The form that is less oxidized has a white colour, while that which is saturated (with oxygen—Author.) is rust-coloured. I have named the first the oxide of cerium *ad minimum* and the second the oxide of cerium *ad maximum*. The oxide of cerium *ad minimum* when placed in the flame of a burner quickly changes to the red variety.”<sup>(3)</sup>

This was a discovery of great importance—one that went to the root of the matter. It established the presence of two valency states in cerium—a fact that was to play a tremendous role later on in the study of the chemistry of the rare-earth elements.

But Vauquelin went further; he made an attempt to separate metallic cerium and one might consider that he was favoured with success, although he himself had doubts about his results.

Finally Vauquelin arrived at the conclusion: “cerium is a peculiar metal, different from all those that are known. It is not an earth.” Unfortunately sufficient attention was not paid to this remark at that time.

Another important observation (for later developments) was made in 1814 by Berzelius, who discovered yttria together with ceria in ochroite.

## 2. Modern Times—New “Earths”

Thus, thanks to the labours of a few brilliant scientists two new chemical elements were obtained<sup>(4)</sup>—yttrium and cerium.

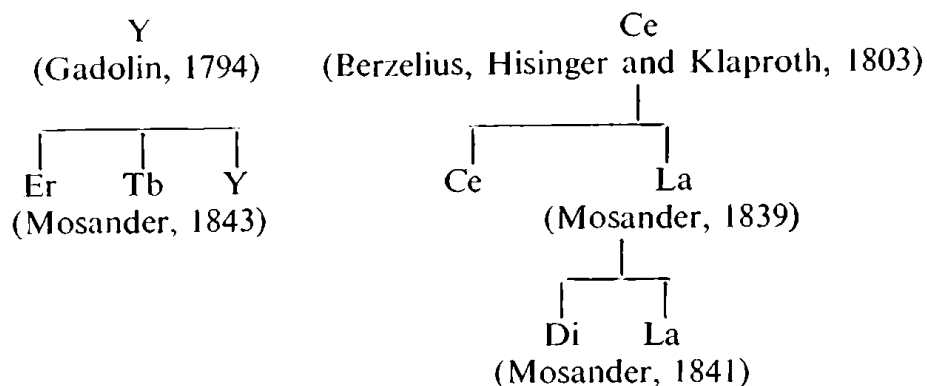
For a long time hardly anyone doubted the separate existence of these. This state lasted till 1839 when a student and colleague of Berzelius, Karl Mosander, became engaged in the investigation of new "earths".

Having decided to verify Vauquelin's statements regarding the two degrees of oxidation of cerium, Mosander calcined cerium nitrate and treated the partially decomposed salt with dilute nitric acid. As was to be expected, cerium, passing over to a higher degree of oxidation as a result of heating, did not dissolve. But in the extract the investigator discovered a new "earth", which he called lanthanum (from the Greek word *lanthanos*—hidden).

The discovery aroused great interest among scientists and posed the following question: If "ceria" which was considered a single substance chemically turned out to be a complex substance, where was the guarantee that lanthanum was a simple substance? The answer to this question was Mosander's discovery in 1841 of a new "earth" separated from lanthanum oxide. The new-born substance so strongly reminded one of its predecessor lanthanum that it was named "didymium" which means "twin".

Scientists were curious to know more and doubts arose as to whether "yttria" was a complex "earth" containing unknown elements. Two more years passed and Mosander was to surprise chemists with the news that "yttria" contained, as he had found, at least three "earths". Ingenious chemist that he was, Mosander applied to a solution of "yttria" the method of fractional basic precipitation with ammonium hydroxide (one of the oldest methods of separating "rare earths") and detected in the first fraction a new yellow "earth", which he called erbia<sup>(5)</sup> and which is the least basic. In the second fraction he found a pink oxide of what he called terbia with intermediate basicity. And finally, yttria itself was found in the third and most basic fraction.

Thus the chain started by Johann Gadolin stretched on. Half a century after the discovery of the Finnish chemist the number of "rare earths" discovered had risen to six. The tortuous path covered may be represented by the following short diagram:



It is difficult to overestimate the significance of the work of Mosander. It is not only that the scientist was able to discover a few new chemical elements. Cases are known in the history of chemistry where the investigation of the properties of some elements in mixtures has led to the discovery of new elements—satellites, as in the case of the platinum metals. With the “rare earths” however, the problem was far more complicated. Two elements, considered chemically distinct, were found to be in fact a mixture of a number of others with unusually similar properties. The case is unique in the history of the discovery of elements. The unusual similarity of the “rare earths” drew the attention of scientists. Berzelius, the greatest analyst of the 19th century, wrote; “Didymium oxide resembles the oxides of lanthanum and cerium so closely in its properties that hardly any other way of separating these oxides is known except that of repeated crystallization of their salts”. And if we are to speak of stages in the history of the chemistry of the rare-earth elements, it is with Mosander’s discovery that a new period begins. Errors and confusions creep in in place of relative clarity.

Let us begin with the fact that Mosander’s work on the separation of “yttria” was subjected to extensive discussion by many chemists. The results obtained by the Swedish investigator were sometimes confirmed while sometimes grave doubts were expressed about them. Finally, the majority of scientists agreed in the opinion that terbia was a mixture of yttria and erbia.<sup>(6)</sup>

The main difficulty in the separation and investigation of the “rare earths”, which possess extremely similar properties, consisted in the absence of sufficiently accurate methods of verification. One of these methods was based on the determination of

the average atomic weight of the fraction separated. This is a classical method, but in the case of virtually identical "rare earths" it was found imperfect, the more so because a particular "rare earth" could not be separated completely and some of the new "earths" discovered by Mosander were subsequently found to be a mixture of elements.

For this reason new methods of analysis—rapid and accurate—which would allow identification of the different "rare earths" were required. And when new optical methods were introduced, the perplexity caused by Mosander's discoveries gave way to a new wave of enthusiasm among scientists.

The method of spectroscopic analysis, invented by Bunsen and Kirchhoff in 1859–1860, was of immense significance for the discovery of the "rare earths". The correctness of Mosander's discoveries, on the whole, was confirmed in the early stages of its application. But, as has not seldom happened in the history of science, the discovery of an advanced method of investigation generated confidence in its infallibility for a certain period, and this confidence later became the source of a number of curious misunderstandings.

### **3. The "Submerged Rock" of the Periodic System**

The periodic law, discovered by D. I. Mendeleyev, established a periodic relation between the properties of chemical elements and their atomic weights and thus served as a strong stimulus for a further careful and thorough study of the properties of elements and their compounds. But like any new law of generalization the periodic system also could not be cast into a logically perfect form immediately. From the moment it was formulated it was faced with the necessity of explaining a number of anomalies which were not in agreement with its internal logic.

One of these problems was that of placing the "rare-earth" elements in the table.

The first difficulty in solving this problem consists in the fact that before 1869 (the year of Mendeleyev's discovery of the periodic law) the rare-earth elements were considered, following Berzelius's example, to be bivalent and the formula of their

oxides was written as  $\text{MeO}$ . It seemed moreover that there was justification for this, since they strongly resembled the alkaline earths in their strong basic character. Another reason for considering rare-earth elements bivalent was the presence of isomorphism between identical compounds of calcium on the one hand, and those of the rare earths on the other. For cerium alone was the presence of the highest oxide " $\text{Ce}_3\text{O}_4$ ", which was considered as  $2\text{CeO} \cdot \text{CeO}_2$ , confirmed, in addition to the oxide " $\text{CeO}$ ." But the oxides of cerium were counted as "earths" and Vauquelin's statement regarding the absence of any "earth"-like characteristic in this element was lost sight of.

D. I. Mendeleev, who was firmly convinced of the correctness of his law, assumed that the rare-earth elements were trivalent. Investigations of the specific heat of cerium and other rare-earth elements and also Cleve's discovery of the isomorphism of the "rare earths" with some trivalent elements confirmed the correctness of the conclusions of the founder of the periodic system.

In addition to this, Mendeleev had to undertake the correction of the atomic weights of the rare-earth elements, the accepted values of which were found to be much lower than what they really were. (See Table 1).

TABLE 1  
*Atomic weights of rare-earth elements corrected by Mendeleev*

Element		Atomic weights	
		Before Mendeleev	Corrected by Mendeleev
Yttrium	Y	60	88
Lanthanum	La	94	138
Cerium	Ce	92	139
Didymium	Di	95	140
Erbium	Er	112.6	175

The establishment of the formula  $\text{Me}_2\text{O}_3$  for the "rare earth" and the revision of their atomic weights was one of the first and

clearest examples of specification of the properties of chemical elements on the basis of the periodic law. But the difficulties were not over yet.

Knowing that the valency of the rare-earth elements is 3 and taking the atomic weights as corrected by Mendeleev, let us try to place these elements in the periodic system.

The position of yttrium does not give rise to any doubts—the element falls in the third group, in the sixth row, between strontium and zirconium. With lanthanum also there is no trouble—it will occupy a position in group III, after barium and below yttrium. Finally cerium can be placed in group IV, after lanthanum. Since in its highest oxide  $\text{CeO}_2$  it is quadrivalent, the valency  $4+$  is characteristic of it to almost the same extent as  $3+$ .

But now comes didymium. It would seem that there is a box free for it in group V, below niobium. But the properties of didymium do not by any means correspond to such a position and attempts to obtain the higher oxide  $\text{Di}_2\text{O}_5$  were not successful. The question of the position of erbium in the periodic system is also far from clear. Mendeleev himself placed the rare earths in the table<sup>(7)</sup> as follows for a long time (Fig. 2).

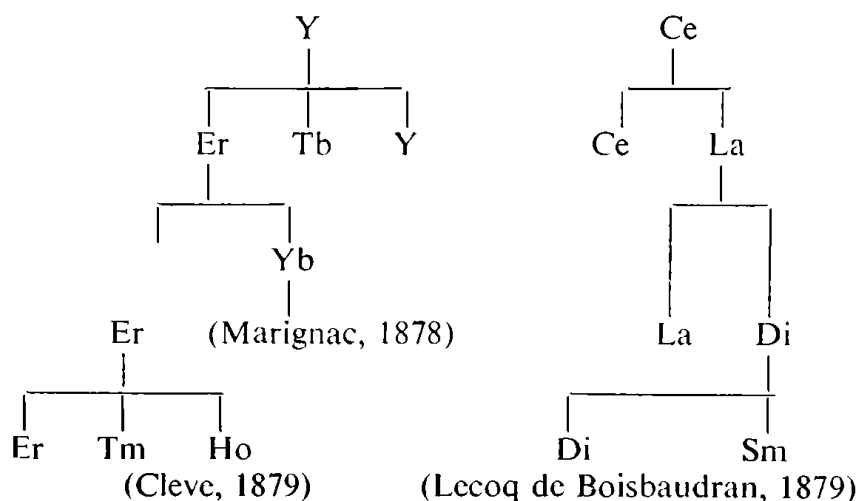
Series	Groups		
	III	IV	V
6	Yt 88	Zr 90	Nb 94
7	In 113	Sn 118	Sb 122
8	La? 138	Ce 139	Di? 142?
9	—	—	—
10	Er 175	? 180	Ta 182

FIG. 2. Arrangement of "rare earths" in the periodic table (Mendeleev, 1877).

By placing a question mark after didymium in group V, Mendeleev indicated that he was not sure that this was the correct position for the element. In later variants of the table Mendeleev excluded all rare-earth elements from it except yttrium, lanthanum and cerium.

Meanwhile the discovery of the periodic law, the development of spectroscopic methods of analysis and the exploration of the possibilities of the electrochemical separation of rare-earth metals all helped the vigorous development of the chemistry of the "rare earths" and led to the discovery of new rare-earth elements. In 1878 Marignac separated first terbium, (thus confirming what Mosander had discovered long ago) and then a new element—ytterbium—in erbium. A year later Cleve demonstrated the complexity of "erbia" by dividing it into erbium proper and two elements unknown earlier—holmium (in honour of Stockholm) and thulium (from Thule, the ancient name of Scandinavia). Finally, in the same year Lecoq de Boisbaudran extracted samarium (named after the mineral samarskite) from didymium.

Thus the scheme of the discovery of rare-earth elements at the beginning of the eighties can be represented as follows:



The eighties brought in new discoveries. The possibility of the practical use of the "rare earths" in incandescent mantles (Auer von Welsbach) posed the problem of working out simple industrial methods for the separation of rare-earth elements from materials found in nature. The chemistry of the "rare earths" thus took the first step from the laboratory towards industry. The practical utilization of the rare-earth elements created the necessity for finding new deposits of raw materials. This also advanced the study of the chemistry of the rare earths to a considerable extent. The results were not slow in appearing.

In 1885 Welsbach separated didymium into two constituents—neodymium and praseodymium (i.e. “new” didymium and “green” didymium, because of the green colour of the salts of the latter). A year later Lecoq de Boisbaudran discovered in samarium the impurity of an unknown element which he called gadolinium, and then extracted dysprosium (“difficult to obtain”) from holmium. The complexity of samarium was demonstrated by the researches of a number of scientists and in 1900 Demarçay discovered the next rare earth—europium.

In the last few years of the 19th century G. Urbain, the French chemist who was later to become one of the greatest specialists in this field, joined in the investigation of the rare-earth elements. Science is indebted to Urbain for his study of the magnetic properties of the rare earths, on the basis of which he proposed a method of identification by their magnetic susceptibility. In 1907 Urbain separated “ytterbia”, earlier isolated by Marignac, into two fractions: neo-ytterbia and lutetia (in honour of the old name of Paris). In 1908 Auer von Welsbach obtained the same result independently by separating aldebaranium and cassiopeium from ytterbium. But the Frenchman had the priority of the discovery.

We have told the story of the discovery of the rare-earth elements in a few pages. We have mentioned only a few carefully verified and confirmed discoveries. But a whole book would be needed if one were to attempt to describe all the wrong clues and the errors on the way to the truth.

Sonorous names like cosmium and neocosmium, austrium and demonium, damarium and lutium, incognitium and victorium—names given to allegedly newly discovered elements which proved to be mixtures of the known elements or represented errors of analysis—would mean little to the reader. Uncritical deference to the ability of spectroscopic analysis played no insignificant role in these innumerable errors. It was only when it was proved that even the slightest impurity affects the position of the lines characteristic of an element in the spectrum that some sobriety set in. One of the reasons for the multitude of false discoveries was the extraordinary similarity of the properties of the “rare earths” and the absence of methods for obtaining oxides of high purity.



But let us return to the question of the position of the rare-earth elements in the periodic system. What is to be done if their number runs into multiples of ten, if Kruss and Nielson announce that there are four components of holmium, three of dysprosium and at least eight (!) of neodymium and praseodymium; if scientists are already tired of inventing new names and confine themselves to signs for denoting newly discovered elements? And is there any limit, after all, to the number of "rare earths"?



D. I. Mendeleev and B. Brauner

Many tried to solve this problem. How are we to explain on the basis of the periodic system the surprising similarity of the properties of the rare-earth elements and conversely, how to place them in Mendeleev's table on the basis of this similarity? It can be said with certainty that most of the modifications of the periodic system were produced by an attempt to solve the problem of placing the "rare earths". The most various forms of the system were proposed: as a curve of dependence of the properties on the atomic weights (in Cartesian co-ordinates); in the form of spirals; in the form of concentric circles; and finally in the form of three-dimensional figures also. But not one of these could be considered successful, since the break in the

continuous periodic sequence of the change in the properties was only masked but by no means removed.

The attempt of W. Crookes to solve the problem of the "rare earths" deserves attention. The distinguished English physicist put forward the concept of the so-called meta-elements in 1886. According to this theory the close similarity of the properties of the rare-earth elements is possibly explained by the fact that they are modifications of one common element and the modifications differ only in their atomic weight and not in their chemical properties. Crookes based himself on the fact that he was able to separate yttria into eight different components with different fluorescence spectra. Similar phenomena were found for some other "earths".

Although it was possible later to establish that the difference in the fluorescence spectra was explained by the impurities of known elements, the hypothesis of meta-elements was an example of the purely intuitive approach to the discovery of the phenomenon of isotopicity.

U. Tommasen and, in particular, Bohuslav Brauner, the Czech chemist who was a friend of D. I. Mendeleyev, came closer to a solution of the problem than the others.

Tommasen quite correctly assumed the number of rare-earth elements "between cerium and the element with the atomic weight 181, which was not finally determined," to be 13, and believed that one of the undiscovered elements must occupy a position between neodymium and samarium.

As regards Brauner, he devoted the greater part of his life to establishing the periodic law on a firm basis and developing it. He pondered over the mystery of the rare-earth elements for a long time in the course of his long and numerous researches in chemistry and finally reached the conclusion that the rare-earth elements should be separated into a very special closed group. This group should be placed at the centre of the periodic system in a large box as a special inter-periodic group. "I consider this group as a continuation of the present fourth group, beginning with cerium and ending with an element, unknown at present, with an atomic weight approximately equal to 180, lying to the left of tantalum", wrote Brauner in 1902. Figure 3 shows the distribution of the elements according to Brauner.

Series	Groups				
	I	II	III	IV	V
Eighth series	Cs 133	Ba 137	La 139	Ce 140	
				Pr 141	
				Nd 144	
				— —	
				Sm 148	
				Eu 151	
				— —	
				Gd 156	
				— —	
				Tb 163	
				Ho 165	
				Er 166	
				— —	
				Tu 171	
				Yb 173	
				? 180	Ta

FIG. 3. Arrangement of "rare earths" in Mendeleyev's table (Brauner, 1902).

But even Brauner's investigations could not finally solve the problem of the rare-earth elements. The periodic law in the stage of its development at the beginning of the 20th century could solve neither the problem of the number of rare-earth elements nor that of their position in the table. The group of rare-earth elements continued to remain as the "submerged rock" of the periodic system.

The position started to clear up only when physics came to the aid of chemistry with its armoury of new methods of investigation.

In 1913 the English physicist Moseley established, on the basis of an analysis of the X-ray spectra of various elements, that the serial number of an element in Mendeleyev's table emitting waves of a given wavelength can be determined from the wavelength of the characteristic X-ray radiation. Moseley's discoveries provided, in point of fact, a general verification of the

periodic law and were at the same time a brilliant new triumph for it.

It was found that the last of the rare-earth elements, lutetium, has the serial number 71, and the next element tantalum the number 73. Hence Moseley's discovery predicted the existence of an unknown element under the number 72.

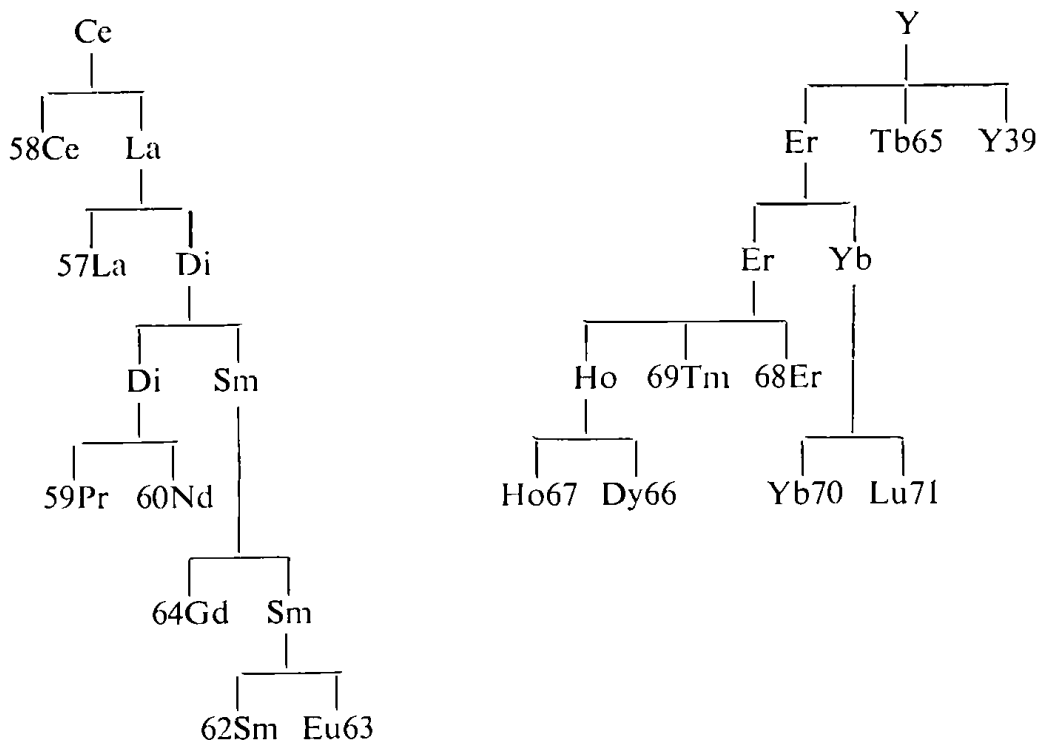
But where does the element as yet undiscovered belong? Is it like its neighbour on the left a member of the family of rare-earth elements or is it an analogue of zirconium, an element of group IV? On the answer to this question depended whether experimental chemists should look for the new element—in zirconium ores or in rare-earth minerals.

Many research workers headed by Urbain supposed that element number 72 should belong to the "rare earths" and looked for it among their compounds; there was even a report of the discovery of the element celtium during the investigation of fractions containing ytterbium and lutetium. Dauvilier stated that he had been able to discover element number 72 in these fractions by the spectroscopic method. But no confirmation of the discoveries supposed to have been made was to follow.

Thus Moseley's discoveries allowed establishing the sequence of arrangement of the rare-earth elements and proved their chemical individuality. But they could not finally solve the problem of their position in the period system and determine which of the rare-earth elements was the last in the group—lutetium or element 72. These obscurities were removed by the Danish physicist Niels Bohr, who developed the theory of the structure of the electron shells of atoms.

From Bohr's theory it followed, as we shall see in the following chapter, that the family of rare-earth elements ends with lutetium, and element 72 is an analogue of zirconium and therefore belongs to the fourth group of the periodic system. Bohr's prediction was soon brilliantly confirmed. In 1923 Koster and Hevesy discovered element 72 in a Norwegian zirconium ore. It was given the name hafnium. Thus the main "submerged rock" of the periodic system was pulled up.

Now we shall return again to the scheme of discovery of the rare-earth elements. We have every right now to give it its final form. We shall write the serial numbers against the symbols.



But excuse me, where is element 61?

Moseley's investigations demonstrated indisputably that an element with this serial number must exist.

It has a very peculiar history . . .

#### 4. The Elusive Element 61

It is difficult to find an element with a "life-history" more peculiar than that of element 61 in the periodic table. The unusual course of events connected with its discovery sets it apart among the lanthanides.

We shall therefore discuss its history in somewhat greater detail.

In April 1926 three American chemists—Harris, Yntema and Hopkins—announced that they had discovered a new element with  $Z = 61$ , which they named illinium (in honour of the state of Illinois). A whole complex of spectroscopic methods was used to detect the element. In their detailed article the authors stated, in particular, that "there were no theoretical grounds for supposing that an element may exist between neodymium and samarium till Moseley's law indicated the possibility of identifying it."

It is impossible not to agree with this statement if the physical basis of the periodic law is borne in mind. Moreover, it would seem that the element between Nd and Sm could not be predicted in the way Mendeleev predicted some other undiscovered elements. In the latter case the discoverer of the periodic table proceeded from a knowledge of the chemical and physical properties of the simple neighbouring elements and the general principle behind the table of elements. In the case of the "rare earths" however, this kind of reasoning led, as we have seen, to a dead end.

But Brauner categorically disagreed with the opinion of these Americans and was quick to comment on the paper on illinium. In his note the Czech investigator of the "continent of rare earths" wrote that he had predicted element 61 long before Moseley's work. In those years the atomic weight of an element used to be its fundamental characteristic. Brauner noticed that the difference between the atomic weights of Nd and Sm was anomalously large (6.1) and such a large difference is not observed between any two neighbouring elements in the periodic system. This led to the idea of the existence of a "gap" in the series of "rare earths" between Nd and Sm. The earliest researches of Brauner on didymium paved the way to such a conclusion. We may note incidentally that it was sheer accident that prevented him from "sub-dividing" didymium three years before Auer von Welsbach.

Brauner's prediction was based on his wonderful knowledge of the chemistry of "rare earths". "My personal knowledge of the chemistry (I consider the spectra to be too confused) of neodymium and samarium led me to the conclusion that there is an unknown element between them", wrote the scientist. His view was reflected in the allocation of the "rare earths" in Mendeleev's table (Fig. 1) given above. A different value for the difference between the atomic weights of Nd and Sm (4) should not cause any confusion, since the atomic weights of the rare earth were being altered and subjected to improvement for a long time because of the difficulties in obtaining pure preparations.

Brauner's forecast is an excellent example of scientific intuition: Determining the exact position of an undiscovered element

in the series of "rare earths" without knowing the actual number of rare-earth elements, merely from an excellent knowledge of their properties and the nature of variation of these.

The existence of an unknown element between Nd and Sm was also assumed by J. Tomsen, a Dane, in 1895 and Van den Brek, a Dutchman in 1912. But their conclusions were apparently based on Brauner's researches.

Moseley's researches stimulated the search for element 61 in nature. It seemed strange that it had not been detected till then. For a period of over 40 years—since the periodic law was established till Moseley's discovery—chemists had analysed many rare-earth minerals and had separated from them all the "rare earths" unknown earlier except one. Element 61 belongs to the first half of the rare-earth family, to the so-called cerium group of the "rare earths". They are more abundant in nature than elements of the yttrium group (the "heavy" rare-earth metals). But all of them, even the rarest members of the yttrium group, were discovered, but not element 61 of the cerium group.

The discovery of illinium was therefore enthusiastically received. It seemed to be confirmed by the researches of other scientists also. Disputes arose regarding the priority of its discovery: Two Italians, Rolla and Fernandes, announced that they had discovered element 61 two years earlier and named it "florentium". Then again, there were determined opponents of the whole idea who were to make cell 61 of Mendeleyev's table empty again.

The German chemist Prandtl examined numerous samples of rare-earth preparations but was unable to discover even a hint of element 61. He concluded that number 61 must be a homologue of manganese. He believed that the "rare earths" should be distributed over the groups of the periodic system. Then number 61 should fall in the UP group, in the Mn subgroup. Manganese was the only known element in this subgroup. All the others, 43, 61, 75 (and 93, before which the discontinuity in the periodic system occurred) were not discovered. Prandtl even detected a certain regularity in the fact and believed that element 61 would hardly be discovered at all. Although his hypothesis could not withstand criticism, he was the first

to note empirically certain resemblances between the elements 43 and 61.

Two other German scientists, Ida and Walter Noddak—studied the X-ray spectra of a large number of preparations in which illinium was supposed to be present. The result was negative. The accuracy of their experiments was such that if element 61 had been 10 million times rarer than Nd and Sm it would have been detected.

But in the mid-twenties the geochemical researches of Vernadskii, Fersman and Goldschmidt showed, as we shall see later, that the “rare earths” were by no means rare. It therefore became difficult to explain the incomprehensible absence of element 61.

It was assumed for a number of reasons that element 61 was geochemically different from the other lanthanides and should be looked for among the rare-earth minerals. The search was not successful. The hypothesis was put forward that element 61, like element 43, was radioactive, but its half-life was much shorter than the period of existence of the earth and the element had disintegrated in the previous geological epochs. This was the view held by Ida Noddak, who supposed that element 61 perhaps stood “in the same relation to samarium as radon to radium”.

At first sight this hypothesis was easy to reject. Firstly, although in some elements with a medium atomic weight (potassium, calcium, rubidium etc.) radioactivity was discovered, only one isotope was found to be unstable, the others were stable. Secondly, the half-lives of these isotopes reached astronomical values (hundreds of trillions of years) and exceeded by several times the period of existence of the earth. There was therefore no reason for supposing that element 61 (and 43) would exhibit such a sharp anomaly in their radioactive properties.

But this was just what proved to be the case. We shall now have to learn a certain rule of nuclear physics first observed in the twenties by the Soviet chemist Shchukarev and formulated definitely in 1934 by the German physicist Mattauch.

We know that modifications of the same chemical element with different atomic weights are called isotopes. If 2 isotopes of



different elements (i.e. with different nuclear charge) have the same atomic weight they are called isobars. Shchukarev and Mattauch's rule states that if there are 2 isobars whose  $Z$  differ by unity, one of them is bound to be unstable.

Let us write out the stable isotopes of neodymium and samarium:

Neodymium	142	143	144	145	146	—	148	—	150	—	—	—	—
Samarium	—	—	144	—	—	147	148	149	150	—	152	—	154

We see that the isotopes of neodymium and samarium occupy the interval of mass numbers 142–154 (the possible “vacancies” for the isotopes  $61^{151}$  and  $61^{153}$  are excluded because they must be, as is clear now, strongly radioactive). None of the isotopes of element 61 can be stable according to the rule. The same can be said about element 43 situated between molybdenum and ruthenium.

It became clear why element 61 had proved to be elusive so long.

Advances in nuclear physics made it possible to obtain it artificially.

In 1937 Pool and Quill observed that isotopes of element 61 are formed on bombarding neodymium with deuterons. Nine years later Marinsky and Glendenin chemically separated the element from fission fragments of uranium produced by neutrons.

The last of the rare-earth elements was named promethium (chemical symbol Pm) in honour of the mythological Titan Prometheus, who stole fire from heaven and gave it to men and was chained to a rock by Zeus as a punishment for this.

The legend says that a vulture used to come and torment him in this state every day. “The name not only symbolizes the dramatic way in which the new element was obtained in appreciable quantities thanks to the harnessing of nuclear energy, but also warns men of the threatening danger of punishment by the vulture of war”—wrote the discoverers of the element.

It was only after the discovery of the periodic law that researches on rare-earth elements became, to a considerable extent, directional in nature.

But as we have seen already, there were many interesting and

important incidents in the history of the rare-earth elements before Mendeleev. Quite a few of them are concerned with Russian scientists. In this connexion it is necessary, first of all, to mention the discovery of a number of minerals containing "rare earths" in Russian territory. Of special importance are the researches of the Russian mineralogist N. I. Koksharov, who described the new minerals found in the Urals in which the presence of "rare earths" was detected, and also the work of Karavaev and Hermann.

As regards the investigation of problems connected with the rare-earth elements in our scientific literature, an eminent position belongs to the distinguished Russian chemist G. I. Hess, the academician from St. Petersburg whose text-book *Principles of Pure Chemistry* ran into seven editions. The material on "rare earths" in the seventh edition (1849) constitutes a detailed review of the properties of the rare-earth elements known at that time (La, Ce, Di, Y, Tb, Er) and their compounds, methods of extracting the "rare earths" from minerals and separating them into their components. Hess particularly emphasizes the extraordinary similarity of their chemical nature and points out the special properties of cerium. Among Hess's contemporaries in Russia, G. Rose and P. Shubin made an experimental study of the rare-earth elements. The latter, a pupil of the academician, determined the atomic weight of lanthanum, a work which won the praise of Berzelius. It is very likely that the work was carried out by Shubin with the knowledge, and under the direction, of Hess.

The end of the 19th and the beginning of the 20th century produced an impressive group of Russian scientists who undertook the experimental investigation of the rare-earth elements—L. G. Melikov, S. M. Tanatar, P. D. Krushchev, G. P. Chernik and others. Considerable attention was paid to the problem of "rare earths" by scientists with a worldwide reputation like L. A. Chugayev and L. V. Pisarzhevskii.

Nikolai Arsent'yevich Orlov (1870–1919) may be considered as the most important figure among Russian investigators of the mysterious "continent of rare earths". A physician by profession, Orlov was also a brilliant analytical chemist and it is difficult to say what was the main achievement in his life. The

excellent work of Orlov in the field of the rare-earth elements speaks for itself. Unfortunately most of it was unpublished and we can only form an idea of them mainly from his correspondence with P. N. Chirvinskii and the review article printed in the *Journal of the Russian Chemical Society* after the death of the scientist. If Orlov did not succeed in founding a school in Russia, like those of Urbain and Marignac in France, Brauner in Czechoslovakia and Prandtl and Muthmann in Germany, the reason lay in the difficult circumstances of his life and the almost complete absence of interest in the study of the rare-earth elements on the part of official science in Tsarist Russia.



N. A. Orlov

To relate Orlov's achievements in the field of the rare-earth elements it is enough to quote a few extracts from one of his letters to P. N. Chirvinskii, dated 18th February 1914. "It seems that this year I shall finish my work on erbia which has lasted for five years." "This work is pure sport, a record of patience, lest we say too proudly that it is a masterpiece of technical procedure . . . After all I have obtained preparations which nobody except Urbain has obtained. The erbium oxide

I have varies in atomic weight on crystallization only in decimal fractions, from 167.3 to 167.5”.

And nobody in those years was able to obtain purer preparations of “rare earths” than those of the French chemist Urbain.

Unfortunately this work was to remain unknown.

To N. A. Orlov belongs the credit for the analysis of many rare-earth minerals. According to the testimony of P. N. Chirvinskii, the scientist had the richest collection of minerals containing “rare earths”.

This eminent Russian scientist had a high opinion of the method of fractional crystallization and introduced many valuable improvements into it. The method of purifying cerium by dissolving salts in an excess of ammonium oxalate and subsequent reprecipitation from solution by the addition of sulphuric acid has retained its importance even to-day.

Orlov's theoretical views on the problem of placing the rare-earth elements in the periodic system are also interesting.

Orlov considered this problem as the principal “submerged rock” of the periodic system. But he clearly defined his attitude towards the various attempts at solving it and accepted Brauner's theory on the arrangement of the rare-earth elements as a special inter-periodic group. He wrote: “Personally I believe in Brauner's theory according to which rare earths with atomic weights from 140 to 175 fill up the entire space from Ce to Ta. In fact it is rather unlikely that the missing members between Mo and W, Nb and Ta, Ru and Os, Rh and Ir, Ag and Au, etc., will be found as the periodic system requires.” “As regards the fact that 10 or more elements occupy in the periodic system a place intended, as it were, for one element, rare-earth elements are not the only ones in this respect. Elements of the eighth group present a similar phenomenon, as do the group of radioactive elements and the final products of their transformation.”

Orlov's name can be unhesitatingly put together with the greatest investigators of the “rare earths”.

Research on rare earth elements developed on a large scale in our country after the October revolution. The geochemical investigations of V. I. Vernadskii and A. E. Fersman helped to demolish the old views on rare-earth elements which held

that they were scarce. Numerous analyses of well-known as well as newly discovered rare-earth minerals were made by I. N. Zaozerskii, I. D. Borneman-Starynkevich, S. A. Borovik, K. A. Nenadkevich, I. P. Alimarin and others. An important event was the discovery of the elements of the cerium group in apatites of Khibin.

Soviet scientists (D. I. Ryabchikov, E. I. Vainshtein, A. N. Zaidel and others) have made important contributions to the processing of rare-earth elements, new methods of isolating and identifying them, and their analysis with the help of physical methods of investigation etc.

### **5. The Role of Russian Scientists in the Study of the Rare-earth Elements**

Our historical survey would be incomplete if we did not describe briefly the role played by Russian scientists in the study of the rare-earth elements.

Scientists belonging to different fields took part in this difficult and painstaking work—chemists and mineralogists, geologists and physicists, biologists and physicians. These researches which were intensified after the victory of the October revolution gained a special impetus in the last decade.

Naturally one must begin with Mendeleyev's contribution to the solution of the problem of rare-earth elements. This contribution is mainly theoretical in nature.

If this scientific genius, relying on his superb intuition, had not decided to change the atomic weights of the elements known at that time, if he had not proposed the formula  $\text{Me}_2\text{O}_3$  instead of the apparently legitimate  $\text{MeO}$ , nobody knows how complicated the solution of the problem of the "rare earths", difficult even otherwise, would have been. But Mendeleyev did not confine himself to correcting atomic weights, he took an active part in the experimental determination of their correct values. In the course of these investigations he observed the difference in the solubilities of the double ammonium nitrates of lanthanum and didymium—a factor which later formed the basis of one of the processes for the separation of the rare-earth elements.

## CHAPTER 2

### WHY IS THE FAMILY OF RARE -EARTH ELEMENTS PECULIAR ?

#### 1. The Periodic System and the Structure of Electronic Shells

Let us turn once again to Mendeleyev's periodic system and calculate the number of elements corresponding to the periods of the table.

In the first, the shortest, there are only two elements—hydrogen and helium. Next come two periods, also short, in which the number of elements is eight. These periods begin with the alkali metals Li and Na and end with the inert gases Ne and Ar respectively. The following periods, the fourth and the fifth (K–Kr and Rb–Xe) are already considerably longer and consist of 18 elements. Finally, in the sixth period (Cs–Rn), which incidentally contains the rare-earth elements in which we are interested, the number of elements increases to 32. The last, the seventh, period beginning with the element 87 is incomplete.

The number of elements in the different periods is given in Table 2.

TABLE 2  
*Number of elements in Mendeleyev's periodic table*

Period	Number of elements in the period	Period	Number of elements in the period
First . (H – He)	2	Fourth . (K – Kr)	18
Second . (Li – Ne)	8	Fifth . (Rb – Xe)	18
Third . (Na – Ar)	8	Sixth . (Cs – Rn)	32

Are these numbers random numbers, or is there some regularity of deep physical significance hidden here? Connected with this question there is another. The periodic system is based on the gradual periodic change in the properties of the elements from the alkali metals to the inert gases. This is clear. But why is it that in some cases (the second and the third periods) this variation occurs over a series of 8 elements while in the longer periods this gradual transition stretches over a considerably large number of elements (18, 32)?

Classical physics and the prevailing view of the structure of atoms could not give a clear answer to these questions.<sup>(8)</sup>

Discoveries of the greatest importance were made at the turn of the 19th century. The discovery of the phenomenon of radioactivity, the mutual transmutability of elements, the creation of quantum mechanics, based on the principle that energy is radiated not continually but in discrete amounts or quanta. These considerations made it possible to reconsider the old view of atomic structure.

In 1911 the English physicist Ernest Rutherford proved the existence of the atomic nucleus with the help of fairly simple but very ingenious experiments. By bombarding thin foils of different materials with  $\alpha$ -particles, the scientist established that many of them pass through the foils without changing their direction, while others undergo a large deflection (Fig. 4).

Hence the mass of the atom, like its positive charge, is not distributed uniformly over the entire volume, for in that case the  $\alpha$ -particles would not have been deflected significantly from their path. In other words, the positive charge is concentrated in a relatively small volume within the atom—in the nucleus of the atom. Since the atom as a whole is neutral, the charge of its nucleus must be compensated by the total negative charge of the electrons situated outside the nucleus.

The atom, which was previously assumed to be impenetrable, in fact turned out to be transparent! It was calculated that the ratio  $\frac{\text{diameter of the atom}}{\text{diameter of the nucleus}}$  amounts to  $\sim 100,000$  and practically the entire mass of the atom is concentrated in the nucleus.

But even more interesting things were discovered later. It was found that the charge of the nucleus of the different atoms was

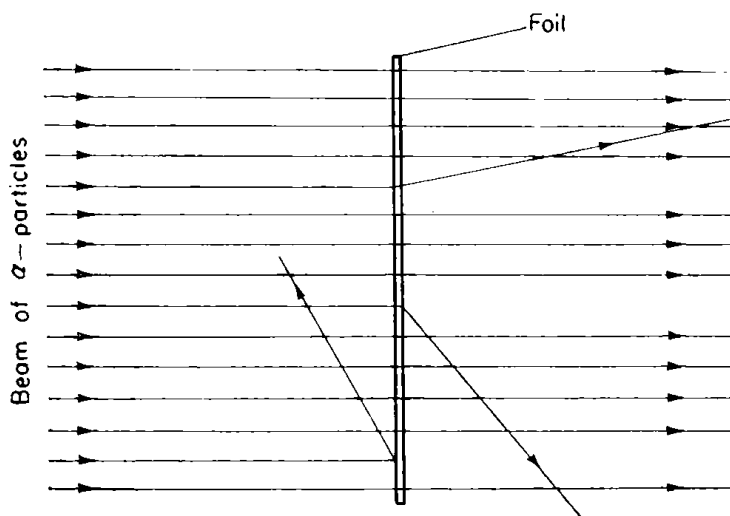


FIG. 4. Scattering of  $\alpha$ -particles by atoms in Rutherford's experiments.

equal to the serial number of the element in the periodic system. For example, the nuclear charge of Li is 3, of La 57, of U 92 and so on. But since the atom is electrically neutral, the charge of the nucleus is equal to the number of electrons, i.e. the number of electrons surrounding the nuclei of the atoms is determined by the serial number of the element.

Rutherford's experiments gave rise to the so-called planetary model of the atom; the atomic nucleus at the centre like the sun in the solar system, and the negative electrons around the nucleus, revolving like planets in their orbits.

But can the electrons revolve in any orbit round the nucleus? This is the problem which Niels Bohr took up when he started to work out his theory in 1912. Underlying this theory were the concepts of quantum mechanics, i.e. it was assumed that the distance of the electrons from the nucleus, and hence also the binding energy of the electron with the nucleus does not vary continuously but in intervals or quanta. To put it more concretely, Bohr proceeded from the following postulate: the electron can revolve round the nucleus only in certain definite "allowed" orbits, and not in any orbit.

These orbits have radii which are related to each other as  $1^2 : 2^2 : 3^2 : 4^2 \dots n^2$ . The quantity  $n$  was later called the principal quantum number; it determines the number of the "allowed" Bohr orbit or, according to modern ideas, of the electron shell.<sup>(9)</sup>



Thus the electrons surrounding the nucleus are arranged in a few electron shells, the electrons of the orbit farthest from the nucleus being most weakly bound to the nucleus. The electrons of the last (or the last but one) orbit are therefore the most mobile and they alone can take part in the formation of a chemical bond between atoms. Hence it follows that the chemical properties of elements are determined mainly by the structure of the outer electron shell of their atoms. This also explains the physical significance of the periodicity of the variation of the properties of the elements. As  $Z$  (atomic number) increases, there is a corresponding increase in the number of electrons and finally we reach the moment when a given electron shell is completed and the filling of the next shell begins. It follows that two elements containing an identical number of electrons in the outer shells should have similar properties.

Thus the number of the external electron shell or the total number of shells surrounding the atomic nucleus of a given element is equal to the number of the period of the table of elements in which the given element is situated. So far-reaching is the significance of the principal quantum number  $n$ .

But it is found that the numbers  $n$  are insufficient for a complete description of the electrons surrounding the nucleus. The "azimuthal" ("secondary") quantum number  $l$ , determining the form of the shell is introduced in addition. This can take integral values from  $n-1$  to 0, i.e. it is connected with  $n$  by the simple relation  $l = n-1$ .

Let us now get acquainted with some notations used in atomic physics which will be useful later.

The principal quantum number  $n$  is denoted by figures, i.e. by  $n = 1, 2, 3$ , etc. or by capital Latin letters:  $K$ -shell ( $n = 1$ ),  $L$ -shell ( $n = 2$ ) etc. The azimuthal quantum number is denoted by small Latin letters  $s, p, d, f$ , etc., instead of 0, 1, 2, 3 . . .

The electrons of the  $K$ -shell are therefore designed as  $1s$ -electrons: for this shell  $n = 1, l = n - 1 = 0$  ( $s$ ). In the  $L$ -shell ( $n = 2$ )  $l$  can take two values: 1 and 0, i.e.  $p$  and  $s$ , and hence the corresponding electrons are designated as  $2p$  and  $2s$ . In the third shell ( $M$ )  $n = 3, l = 2, 1, 0$ , i.e.  $d, p, s$  ( $3d, 3p, 3s$ -elec-

trons); In the fourth ( $N$ )  $n = 4$ ,  $l = 3, 2, 1, 0$ , i.e.  $f, d, p, s$  ( $4f$ -,  $4d$ -,  $4p$ - and  $4s$ -electrons) etc.

Since both the atom and the electron possess magnetic properties, this should be reflected in the different states of the electron even when  $l$  and  $n$  are equal (since in this case the shells may be differently oriented). The third quantum number is introduced to take this fact into consideration:  $m_l$  — the orbital magnetic moment, or as it is called, the magnetic quantum number, which also can take only integral values, positive or negative:  $+l, +(l-1) \dots 0 \dots -(l-1), -l$ , i.e.  $m = 2l + 1$ . For example, if  $l = 3$ ,  $m_l$  can take  $2 \times 3 + 1 = 7$  different values.

The magnetic properties of the electron, arising as a result of the rotation of the electron around its own axis, are characterized by the fourth quantum number ( $m_s$ ), which takes two values:  $+\frac{1}{2}$  and  $-\frac{1}{2}$ , depending on the direction of rotation of the electron.

Thus 4 quantum numbers are required for the complete description of an electron in an atom:  $n$ —the principal quantum number,  $l$ —the azimuthal quantum number,  $m_l$ —the orbital magnetic moment and  $m_s$ —the spin of the electron.

The Swiss physicist Pauli put forward the hypothesis: No 2 electrons in an atom can have 4 identical quantum numbers. The order of distribution of the electrons in the different electron shells is based on this fundamental principle.

It will be remembered that the number of an electron shell corresponds to the period in Mendeleyev's periodic system. Hence Pauli's principle determines the number of elements in each of the periods.

Let the azimuthal quantum number be equal to  $l$ . Since we have to take into consideration the magnetic quantum number which can take  $2l + 1$  values, we get  $2l + 1$  values different states for the electrons in the atom for  $l$ . Since the fourth quantum number also has to be considered, and it can take 2 values ( $+\frac{1}{2}$ ), this number of states has to be doubled:  $2(2l + 1)$ . Therefore, there can be  $2(2l + 1)$  electrons with different  $l$  for the principal quantum number  $n$ .

Let us take  $n = 1$  ( $K$ -shell). Then  $l = 0$ . Hence,  $2(2l + 1)$ ,  $= 2(2 \times 0 + 1) = 2$ , i.e. in the first electron shell there are 2

electrons which are 2 *s*-electrons. This is usually written:  $1s^2$ . This means that in a shell with  $n = 1$  there are 2 *s*-electrons.

Let us move on to the *L*-shell. Here  $n = 2$ ;  $l$  can therefore take the 2 values 0 and 1. For  $l = 0$  we have already established the presence of 2 *s*-electrons. For  $l = 1$ ,  $2(2l + 1) = 2(2 \times 1 + 1) = 6$ , i.e. 6 *p*-electrons correspond to this value of  $l$ . Thus in the second electron shell there are 2 *s*-electrons and 6 *p*-electrons, 8 in all. In an abbreviated form:  $2s^2 p^6$ .

From similar considerations we find that for  $l = 2$  (*d*-electrons),  $2(2l + 1) = 10$ ; for  $l = 3$  (*f*-electrons),  $2(2l + 1) = 14$  etc.

Thus we have found the number of electrons in the different shells:

in the first	$(n = 1): 2$ ( <i>s</i> -electrons);
in the second	$(n = 2): 2 + 6 = 8$ ( <i>s</i> - and <i>p</i> -electrons);
in the third	$(n = 3): 2 + 6 + 10 = 18$ ( <i>s</i> -, <i>p</i> -, and <i>d</i> -electrons);
in the fourth	$(n = 4): 2 + 6 + 10 + 14 = 32$ ( <i>s</i> -, <i>p</i> -, <i>d</i> - and <i>f</i> -electrons);
in the fifth	$(n = 5): 2 + 6 + 10 + 14 + 18 = 50$ ( <i>s</i> -, <i>p</i> -, <i>d</i> -, <i>f</i> -, and <i>g</i> -electrons); etc.

Let us now turn to Table 2; it is obvious that the number of elements in the periods coincides with the number of electrons in the different ( $n = 1, 2, 3, 4, \dots$ ) electron shells. We have therefore found the answer to the first of the problems posed: the number of elements in the periods is not accidental but reflects a physical regularity of deep significance: the filling of the electron shells.

To answer the second question we shall have to consider the order of filling of the electron shells while passing from the light elements of the periodic system to the medium and then to the heavy ones.

We have found that the first electron shell (*K*) contains only 2 *s*-electrons. The atom of H therefore has 1 *s*-electron ( $1s$ ), the atom of He—2 *s*-electrons ( $1s^2$ ). Hence in the first period there can be only 2 elements. It should be noted here that a shell containing 2 electrons is very stable.

Let us now pass on to the second shell (*L*); it starts filling up with the lithium atom. This atom already has a completed

*K*-shell and an *s*-electron will appear in the *L*-shell, i.e. the electronic structure of Li can be written as  $1s^2 2s$ . The structure of the following element, Be, will be  $1s^2 2s^2$ . Later, the *L*-shell is filled at the expense of the 6 *p*-electrons and is completed in the inert gas neon ( $1s^2 2s^2 p^6$ ). The second period of the periodic system, containing 8 elements, ends with neon. A shell with 8 electrons is also very stable.

The third period begins with the alkali metal sodium in which the 3*s*-electron appears. The structure of the sodium atom is  $1s^2 2s^2 p^6 3s$ , that of the next element, magnesium, is  $1s^2 2s^2 p^6 3s^2$ . Then the *p*-electrons again come into the picture, the inert gas argon, with which the period ends, has the structure  $1s^2 2s^2 p^6 3s^2 p^6$ . The third period thus contains 8 elements.

In the fourth period everything goes smoothly up to calcium ( $1s^2 2s^2 p^6 3s^2 p^6 4s^2$ ). But from scandium onwards it is not the fourth shell (*N*) which is filled, as one should expect, but the previous *M*-shell. This shell, as is known, should contain 18 electrons. Since the places for the *s*- and *p*-electrons in it are already occupied, it is filled with the 10 *d*-electrons, the filling being completed with zinc— $1s^2 2s^2 p^6 3s^2 p^6 d^{10} 4s^2$ . After zinc the filling of the *N*-shell continues at the cost of the 6 4*p*-electrons. Thus the fourth period contains 18 elements, ending with the inert gas krypton:  $1s^2 2s^2 p^6 3s^2 p^6 d^{10} 4s^2 p^6$ .

On passing to the fifth period, we observe the appearance of 5*s*-electrons in rubidium and strontium. From yttrium onwards a pattern similar to that of the fourth period is repeated—the *N*-shell starts filling up with *d*-electrons. It ends with cadmium which has the structure:  $1s^2 2s^2 p^6 3s^2 p^6 d^{10} 4s^2 p^6 5s^2$ , and then the 6 5*p*-electrons continue the filling. As a result the structure of the last 2 shells of xenon, the last element of the period, is as follows:  $4s^2 p^6 d^{10} 5s^2 p^6$ .

Now we enter the sixth period and would ask the reader to pay special attention to it for it contains the family of rare-earth elements. This is the longest of the periods we have thus far met and contains 32 elements. Again the first elements of period, Cs and Ba, behave “normally”—6*s*-electrons appear in them.

In lanthanum ( $Z = 57$ ) the order we are used to is continued and the next electron (1 5*d*-electron) is added to the fifth shell.

From cerium onwards ( $Z = 58$ ) the analogy with the fourth and fifth periods breaks down: the electrons begin to fill the fourth shell which lies deeper down. Since it should contain 32 electrons and 18 of them ( $4s^2 p^6 d^{10}$ ) are already in their places, 14 electrons ( $f$ -electrons) are necessary to complete it. This process of completing the fourth shell with the 14  $4f$ -electrons occurs in the family of the lanthanides. The last of these, lutetium, has the structure  $4s^2 p^6 d^{10} f^{14} 5s^2 p^6 d 6s^2$ . The completion of the fifth shell with  $d$ -electrons begins with hafnium and continues right up to mercury<sup>(10)</sup>. The sixth period is completed with radon with the structure  $4s^2 p^6 d^{10} f^{14} 5s^2 p^6 d^{10} 6s^2 p^6$ .

The question of the structure of the seventh period is very complicated and we shall take it up in the last chapter. We now face another problem—to discuss briefly the relation between the structure of the electron shells and the chemical properties of the elements.

We have already drawn the reader's attention to the fact that the valency of elements is connected with the structure of the outer electron shells. We also pointed out that outer shells containing 2 (in He) or 8 electrons are noted for their stability—they are characteristic of the inert gases. Anybody with some knowledge of chemistry knows that chemical names are not given arbitrarily: as a matter of fact the inert gases are practically incapable of forming compounds with other elements. They are said to have zero valency. All the other elements tend to acquire the structure of the nearest inert gas. When this is attained one can speak of the most characteristic valency of the elements.

Let us illustrate what has been said with examples.

In a common compound like ammonia  $\text{NH}_3$ , nitrogen has a negative valency  $-3$ . This means that to attain the structure of the inert gas neon it would require 3 electrons. In the language of atomic physics the following process takes place:  $1s^2 2s^2 p^3$  (structure of the neutral  $N$  atom)  $+ 3\bar{e} \rightarrow 1s^2 2s^2 p^6$  (structure of the ion  $\text{N}^{3-} =$  structure of Ne).

Let us take another compound of nitrogen—nitrogen peroxide  $\text{N}_2\text{O}_5$ . Here 5 electrons must be given to nitrogen ( $\text{N}^{5+}$ ) for it to acquire the structure of the inert gas helium:  $1s^2 2s^2 p^3 - 5e \rightarrow 1s^2$  (structure of He).

The number of electrons in the outer shell increases from left to right within the short periods of Mendeleyev's system. Since the alkali metals have one  $s$ -electron each in the outer shell, the alkaline earths—2  $s$ -electrons each etc. and so on up to the halogens, which have 7 ( $s^2 p^5$ ) electrons. Hence it is evident that the first few elements of a period give up their electrons easily while the last few acquire them in order to attain the structure of an inert gas. The former are characterized by metallic properties, the latter exhibit non-metallic properties.

Now we can understand the period variation in the properties of the elements from those characteristic of metals to those characteristic of non-metals as one moves from the beginning of the period to the end.

In the long periods this change “stretches” over a large number of elements. As we have seen already, in the long periods the filling of the outer electron shells is temporarily interrupted and the 10  $d$ -electrons enter the penultimate shell (the intervals Sc–Zn, Y–Cd), while the external shell remains unchanged. Since the penultimate shell determines the chemical properties to a considerably smaller extent (lower mobility of the electrons as a result of tighter binding to the nucleus) than the outer shell, these elements differ less in their chemical properties. In the sixth period however, in addition to the “inserted 10” there are 14 more elements in which the difference in the electronic structure appears only in the third shell from outside (the successive entry of the 14  $4f$ -electrons). This shell has a very small influence on the chemical properties of the elements, which explains the extraordinary resemblance of the rare-earth elements among themselves.

The development of Bohr's theory and the establishment of Pauli's principle made it possible to solve the problem of the structure of the electron shells of the atoms and thus explain the physical significance of Mendeleyev's periodic system. But for all its importance Pauli's principle only allowed establishing the maximum number of electrons in the energy shells and subshells in an atom. It could not explain why there are 2 periods, and not one, containing 8, 18, etc. electrons each respectively in the periodic system or determine the order of filling of the

free places in an atom with electrons. Thus, for example, with Pauli's principle it was impossible to get an answer to the question why, in cerium ( $Z = 58$ ), instead of the electrons continuing to enter the  $5d$ -subshell, the  $4f$ -subshell starts filling up. In other words, one could not get a physical interpretation of the existence of the family of lanthanides.

This could be done only as a result of later researches. Without going into their subject matter, we shall only mention that in the case of the family of lanthanides it was shown quite definitely that when  $Z = 58$  (i.e. for a nuclear charge corresponding to the element cerium) the filling of the  $4f$ -subshell is of greater advantage, from the point of view of energy, than that of the  $5d$ -subshell, although the former lies deeper down.

Let us come back again to the quantum numbers we already know. The reader will remember that the value of the orbital quantum number determines the appearance of  $s$ -,  $p$ - and  $d$ -subshells. Thus, when  $l = 0$ , there is only an  $s$ -subshell in the atom; when  $l = 1$ , the  $p$ -subshell can come in; when  $l = 2$ , we observe the  $s$ -,  $p$ - and  $d$ -subshells; and finally when  $l$  is equal to 3, the  $f$ -subshell appears and so on. All this is deduced very easily from Pauli's principle. But it could not establish the "critical" atomic number at which a new subshell corresponding to a given  $l$  appears. The theoretical researches of a number of scientists made it possible to propose a short and convenient formula for determining the order in which the subshells are filled.

$$Z_l = \gamma_a (2l + 1)^3$$

where  $l$  is the orbital quantum number, equal to 1, 2, 3, . . .  $Z$  is the serial number of the atom in which a new subshell appears;  $\gamma_a$  is an empirical constant equal to 0.169.

Let us apply this formula in practice;

$$Z_1 = 0.169 (2 \cdot 1 + 1)^3 \approx 5$$

$$Z_2 = 0.169 (2 \cdot 2 + 1)^3 \approx 21$$

$$Z_3 = 0.169 (2 \cdot 3 + 1)^3 \approx 58$$

The numbers obtained, 5, 21, and 58, as can be easily seen from a glance at the periodic table, correspond to the serial numbers of the elements boron ( $Z = 5$ ), scandium ( $Z = 21$ )

and cerium ( $Z = 58$ ), i.e. just those elements in which a new electron shell appears, corresponding to a given  $l$ . The filling of  $2p$ - begins with boron ( $l = 1$ ), that of  $3d$ - with scandium ( $l = 2$ ), and finally that of  $4f$ - with cerium ( $l = 3$ ).

## 2. The Properties of the Rare-earth Elements in the Light of Their Electronic Structure

Now that we are acquainted with the principles of the construction of electron shells in atoms, we can investigate the influence of the characteristic electron configurations of rare-earth elements on their chemical properties. To start with, we shall give the electron configurations of the rare-earth elements in a separate table (Table 3). The distribution of electrons in the shells of barium and hafnium are also given as these are the

TABLE 3  
*Electron configurations of Ba, Hf, and the rare-earth elements*

Serial No.	Symbol	N-shell ( $n = 4$ )				O-shell ( $n = 5$ )				P-shell ( $n=6$ )
		$s$	$p$	$d$	$f$	$s$	$p$	$d$	$f$	$s$
56	Ba	2	6	10		2	6			2
57	La	2	6	10		2	6	1		2
58	Ce	2	6	10	1	2	6	1		2
59	Pr	2	6	10	2	2	6	1		2
60	Nd	2	6	10	3	2	6	1		2
61	Pm	2	6	10	4	2	6	1		2
62	Sm	2	6	10	5	2	6	1		2
63	Eu	2	6	10	6	2	6	1		2
64	Gd	2	6	10	7	2	6	1		2
65	Tb	2	6	10	8	2	6	1		2
66	Dy	2	6	10	9	2	6	1		2
67	Ho	2	6	10	10	2	6	1		2
68	Er	2	6	10	11	2	6	1		2
69	Tm	2	6	10	12	2	6	1		2
70	Yb	2	6	10	13	2	6	1		2
71	Lu	2	6	10	14	2	6	1		2
72	Hf	2	6	10	14	2	6	2		2



elements between which the family in which we are interested is situated.

The order in which the  $N$ -shell is filled with  $4f$ -electrons is clearly represented in the table.<sup>(11)</sup>

We have already made frequent use of the terms,  $f$ -electrons,  $d$ -electrons etc. In conformity with the concepts of atomic physics, we shall consider the electron shells as consisting of subshells. Thus, for example, the  $N$ -shell consists of the  $s$ -,  $p$ -,  $d$ - and  $f$ -subshells. The family of rare-earth elements is therefore characterized by the filling of the  $4f$ -subshell.

When we speak of "rare-earth elements", in addition to the " $4f$ -elements" (as they are often called) we include in this definition lanthanum also. Although spectroscopic data reliably indicates that the first  $4f$ -electron appears in cerium, one is perfectly justified in considering the properties of the 15 elements together, instead of taking lanthanum and the lanthanides separately. In its chemical properties lanthanum is almost identical with the other elements of the rare-earth family. This fact, among others, clearly indicates how small is the influence exerted on the properties of the lanthanides by a change in their electronic configuration due to the formation of the  $4f$ -subshell which lies deep below.

It would be incorrect however to assert that no change at all in the chemical properties occurs through the entire series of the rare-earth elements. Even Vauquelin had noted the anomaly in the properties of cerium, consisting in the two degrees of its oxidation. This was subsequently explained by the existence in cerium of two approximately equal valencies,  $3+$  and  $4+$ . Of course, from lanthanum to lutetium a certain change in the properties takes place due to the increase in nuclear charge. It should be pointed out that not all the properties of the rare-earth elements in the series La-Lu exhibit a change in one direction only. The family of rare-earth elements is a good example of the presence of so-called secondary periodicity.

Secondary periodicity in the family of rare-earth elements is of a somewhat different nature and is expressed mainly in the alteration of anomalous frequencies. Let us consider this question in greater detail.

As is already clear from what has been said, elements, on

entering into chemical combination, tend to acquire the structure of the nearest inert gas by giving up or capturing electrons. The ion of an element with the structure of an inert gas therefore expresses the most characteristic valency of the given element. The fundamental valency of lanthanum is  $3+$ , where the structure of xenon is attained  $4s\ p\ d\ 5s\ p$ . The lanthanides also are trivalent but the structure of the ions with charge 3 differ from that of xenon in having  $4f$ -electrons.

Further, for each electron there is a characteristic binding energy, depending on the subshell in which it is situated. Theory shows that the  $4f$ - and  $5d$ -subshells lie quite closely to one another. This is the reason why the energy of transition of an electron is nearly equal to the energy of the chemical bond. In other words, for the first few lanthanides the  $4f$ -electrons can be used as valency electrons and thus for attaining the structure of La or that of xenon.

From Table 3 it follows that the  $4f$ -subshell is half-filled in gadolinium ( $Z = 64$ ). It is found that the electronic structure of gadolinium with 7  $4f$ -electrons is very stable. It is an "inert gas" structure of its own kind for the series of lanthanides. Incidentally this fact has a very simple physical explanation. Since the principal quantum number corresponds to  $2l + 1$  different states of the electrons (taking the orbital magnetic moment into consideration), for  $l = 3$  we have  $2l + 1 = 7$ . But  $l = 3$  characterizes  $f$ -electrons. Hence, considering  $m_l$ , but not  $m_s$  (the spin quantum number or spin), we have here 7  $4f$ -electrons. But if the spin is taken into consideration we have again as many  $4f$ -electrons. Thus the difference between the first and second set of 7 electrons consists in the different spins—the spins of the former are anti-parallel to those of the latter. In other words, the direction of rotation of the first and second 7 electrons about themselves are opposite.

This forms the physical basis of the division of the rare-earth elements into the cerium group (Ce, Pr, Nd, Pm, Sm, Eu, Gd) and the yttrium group (Tb, Dy, Ho, Er, Tm, Yb, Lu). If we look at the diagram showing the order of discovery of the rare-earth elements (p. 16), we shall find that it breaks up into two parts, one of which shows the order of discovery of the cerium group, and the other that of the yttrium group of rare-earth

elements. It is the well-known difference in the properties of the "light" and the "heavy" rare-earth elements (as the elements of the cerium and yttrium groups respectively are often called) which was responsible for the fact that elements tracing their beginning, so to speak, to yttrium formed one group, while the products of the successive disintegration of the cerium "earths" formed another. In other words, the long-established division of the "rare earths" into the cerium and yttrium groups was an example of a purely intuitive grouping, based on insignificant differences in the properties, towards a more fundamental regularity in the series of the "rare earths". It reminds one how Brauner with his "inter-periodic" group closely approached a solution of the problem of placing the rare-earth elements in Mendeleyev's periodic table.

But, strictly speaking, from the purely chemical point of view the demarcation between the elements of the yttrium and cerium groups is not a sharp one. Thus, for example, europium is rarely classed together with elements of the yttrium group.<sup>(12)</sup>

But let us return to the electronic configuration of the rare-earth elements. It is found that the structure of lutetium, the last of them, with a completed  $4f$ -subshell, is also very stable. If the structure of Gd, as mentioned above, plays the role of a kind of "inert gas" for the neighbouring elements of the cerium and yttrium groups, the structure of lutetium plays a similar role for the elements of the yttrium group.

It is interesting that Meyer, on the basis of chemical data alone, pointed out the unusual similarity in the properties of La, Lu and Gd, long before the problem of placing the rare-earth elements was solved. On arranging the rare-earth elements in two rows and taking into account the existence of two groups and the unusual stability of the electronic structures of  $\text{La}^{3+}$ ,  $\text{Gd}^{3+}$  and  $\text{Lu}^{3+}$ , we get a curious "periodic system" of the ions of the rare-earth elements (Fig. 5).

The existence of anomalous valencies (i.e. other than  $3+$ ) in some lanthanides is due to the presence of three stable electronic structures in the series of rare-earth elements. This is a result of the tendency of these lanthanides to acquire a structure similar to that of  $\text{La}^{3+}$  or  $\text{Gd}^{3+}$  or  $\text{Lu}^{3+}$ .

Let us consider the first group of our peculiar periodic system,

I	II	II	IV	V	VI	VII
						$\text{La}^{3+}$ $5s^2p^6$
$\text{Ce}^{3+}$ $4f^15s^2p^6$	$\text{Pr}^{3+}$ $4f^25s^2p^6$	$\text{Nd}^{3+}$ $4f^35s^2p^6$	$\text{Pm}^{3+}$ $4f^45s^2p^6$	$\text{Sm}^{3+}$ $4f^55s^2p^6$	$\text{Eu}^{3+}$ $4f^65s^2p^6$	$\text{Gd}^{3+}$ $4f^75s^2p^6$
$\text{Tb}^{3+}$ $4f^85s^2p^6$	$\text{Dy}^{3+}$ $4f^95s^2p^6$	$\text{Ho}^{3+}$ $4f^{10}5s^2p^6$	$\text{Er}^{3+}$ $4f^{11}5s^2p^6$	$\text{Tm}^{3+}$ $4f^{12}5s^2p^6$	$\text{Yb}^{3+}$ $4f^{13}5s^2p^6$	$\text{Lu}^{3+}$ $4f^{14}5s^2p^6$

FIG. 5. Periodic systems of the ions of the rare-earth elements.

consisting of cerium and terbium. The valency of cerium,  $4+$ , is characteristic for the element. Cerium gives up its only  $4f$ -electron and acquires the structure of  $\text{La}^{3+}$ . In the same way,  $\text{Tb}^{4+}$  has the configuration of gadolinium, but the quadrivalent state is far less characteristic of terbium.

Two tendencies begin to compete in the case of praseodymium. On the one hand, there appears a tendency of praseodymium to attain the structure of  $\text{La}^{3+}$  by giving up two  $f$ -electrons, on the other hand there is a tendency for the charge to increase. The increasing interaction between the  $4f$ -electrons themselves does not facilitate yielding the electrons. For this reason, the valency state  $4+$  is far less characteristic of praseodymium than of cerium.<sup>(13)</sup> As far as the derivatives of  $\text{Pr}^{5+}$  are concerned, the preparation of  $\text{Pr}_2\text{O}_5$  should be considered very problematic, although theoretically praseodymium can acquire a valency of  $5+$ —the highest possible valency in the lanthanide family. For dysprosium, the analogue of praseodymium, the state  $4+$  has not yet been found and is hardly attainable, since  $Z$  exercises the prevailing influence here.

Elements of the “third” and “fourth” groups, i.e. Nd and Ho,

Pm and Er do not exhibit anomalous valencies—it is impossible for them to attain the structure of  $\text{La}^{3+}$  and  $\text{Gd}^{3+}$ . It is true that Brauner and others reported that they had obtained  $\text{Nd}^{4+}$  but these reports remained unconfirmed.\*

An anomalous valency of  $2+$  appears in samarium, but it is attained not by losing but gaining an electron. The structure of  $\text{Gd}^{3+}$  is not attained, it is true, since for this purpose two whole electrons would be needed. But there is no mention of the derivatives of  $\text{Sm}^+$  in literature. The bivalent state is theoretically possible for thulium, but is not observed in practice,  $\text{Eu}^{3+}$  and  $\text{Yb}^{3+}$  are comparatively easily reduced to the bivalent state: the tendency to attain the stable structures of  $\text{Gd}^{3+}$  and  $\text{Lu}^{3+}$  respectively is a marked one in this case.

The various valency states of the rare-earth elements are shown in Fig. 6.

Some interesting calculations were made on the basis of investigations on the para-magnetic properties of the rare-earth elements. It was found that in the metallic state cerium consists of 20%  $\text{Ce}^{4+}$  and 80%  $\text{Ce}^{3+}$ ; praseodymium and neodymium of 10%  $\text{Me}^{4+}$  and 90%  $\text{Me}^{3+}$  respectively. Samarium contains 20%  $\text{Sm}^{2+}$ . For metallic ytterbium the principal component is  $\text{Me}^{2+}$ .

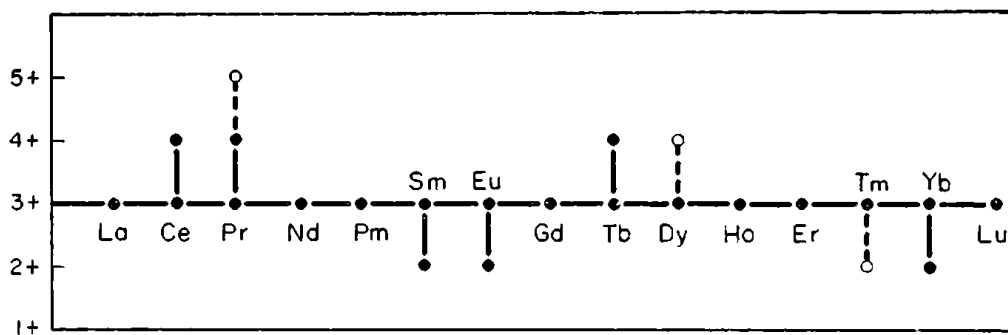


FIG. 6. Scheme of valency states of rare-earth elements.  
— — — O supposed valency states.

But we have to answer another question. At the very beginning of the book we mentioned that yttrium is counted among

\*L. Asprey at Los Alamos Laboratories has produced later evidence for the existence of  $\text{Nd}^{1+}$  and  $\text{Dy}^{1+}$ , while Z. Kiss has demonstrated bivalent states for Tb, Dy, Ho, Er, Tm, Lu.

the rare-earth elements because of the similarity of its properties with the properties of the 15 lanthanides. Finally, as the history of the discovery and isolation of rare-earth elements shows, yttrium is found with them in the same minerals, it enters into many similar reactions and, as we have observed, is nearer in its properties to the "heavy" lanthanides than to the "light" ones. This behaviour of yttrium is not accidental and is explained by the size of its ionic radius. Let us compare the radii of the  $\text{Me}^{3+}$  (in Ångström units,  $1\text{Å} = 10^{-8}\text{ cm}$ ) for the rare-earth elements (Table 4).

TABLE 4  
*Ionic radii of trivalent rare-earth elements*

Serial Number	Element	Ionic radius	Serial Number	Element	Ionic radius
57	Lanthanum . .	1.22	65	Terbium . .	1.09
58	Cerium . .	1.18	66	Dysprosium . .	1.07
59	Praseodymium . .	1.16	67	Holmium . .	1.05
60	Neodymium . .	1.15	68	Erbium . .	1.04
61	Promethium . .	(1.14)	69	Thulium . .	1.04
62	Samarium . .	1.13	70	Ytterbium . .	1.00
63	Europium . .	1.13	71	Lutetium . .	0.99
64	Gadolinium . .	1.11			

The ionic radius of yttrium is  $1.06\text{ Å}$ , it falls in the interval between  $r_{\text{Dy}}$  and  $r_{\text{Ho}}$ . This is the reason for its close resemblance to the rare-earth elements. In processes of isolating the latter, yttrium very frequently appears in some fractions with the middle elements of the yttrium group. In the case of scandium, which also is included with the rare-earth elements, there is already much less similarity. Its atomic radius ( $0.83\text{ Å}$ ) lies far beyond the limits of the atomic radius of the last rare-earth element, lutetium.

Continuing to analyse our table we find that the uniform change in ionic radii of trivalent rare-earth elements breaks down in 3 instances: in passing from La to Ce ( $1.22\text{--}1.18$ ), from Sm to Eu ( $1.13\text{--}1.13$ ) and from Er to Tm ( $1.04\text{--}1.04$ ),

In the first instance, the large difference in the sizes of the atomic radii can be explained by the appearance of a new subshell (the first  $4f$ -electron) in cerium. This is reflected in the well-known difference in the chemical properties of La and Ce, which is somewhat larger than that in the series La–Lu as a whole.

Before trying to explain the two other variations let us make ourselves familiar with the concept of “lanthanide contraction”. This is most easily done as follows.

The lanthanides are situated in the series of elements between lanthanum ( $Z = 57$ ) and hafnium ( $Z = 72$ ). Their analogues in the fifth period of the periodic system are yttrium ( $Z = 39$ ) and zirconium ( $Z = 40$ ). Let us compare the atomic radii of these (in Å):

Y	Zr	La	Hf
1.80	1.58	1.86	1.57

As we see, the radii of Y and La, and of Zr and Hf respectively, almost coincide, although there are no other elements between Y and Zr while there are 14 between La and Hf. Consequently, over the entire series of lanthanides there is a gradual, uniformly small change in the atomic as well as the ionic ( $\text{Me}^{3+}$ ) radii. The reason for such a slow change is that the  $4f$ -subshell and the outer valence shell exert a certain screening effect upon each other. The increase in  $Z$  has only a small effect on the forces of attraction between the nucleus and the outer electron shell and is therefore not accompanied by a marked decrease in the radius. This effect is known as the “lanthanide contraction”.\* It is interesting to note that it has a strong effect on the elements following the lanthanides in the sixth series. These elements closely resemble their analogues in the fifth series for this reason. It is enough to compare the radii once more in order to explain the very great similarity between Zr and Hf, Nb and Ta, Mo and W, Tc and Re, which is considerably greater than that

\*Transliteration here is difficult. In actual fact the lanthanide contraction is highly significant because it places hafnium, zirconium, etc., in the same size range as lanthanum even though 14 electrons have been added. Effectively then, by adding electrons to the  $4f$  shell we find an increased nucleus–electron attraction only part of which is transferred to the outer electron shell.

Zr 1.58	Nb 1.47	Mo 1.40	Tc 1.36	
Hf 1.57	Ta 1.47	W 1.41	Re 1.37	etc.

between Ti and Zr, V and Nb, Cr and Mo, Mn and Tc, because the radii of the atoms of Ti (1.45), V (1.36), Cr (1.28), Mn (1.31) respectively are much smaller.

The close resemblance of the properties of the rare-earth elements and their simultaneous occurrence in nature is explained by precisely these small differences in the sizes of the  $\text{Me}^{3+}$ . As far as the absence of a difference between  $r_{\text{Sm}^{3+}}$  and  $r_{\text{Eu}^{3+}}$ ,  $r_{\text{Er}^{3+}}$  and  $r_{\text{Tm}^{3+}}$  is concerned, the proximity of the stable electronic configurations of  $\text{Gd}^{3+}$  and  $\text{Lu}^{3+}$  exercises an influence here and this probably affects the screening action of the 4f-electrons.<sup>(14)</sup>

### 3. A Brief Account of the Geochemistry of the Rare-earth Elements

The history of the rare-earth elements completed 165 years in 1959, if we take it to begin with Johann Gadolin's separation of "yttria". But the history of minerals containing "rare earths" is considerably longer. It also has covered a long and tortuous path from the discovery of some exceedingly rare minerals, at times only museum pieces, to the discovery of abundant deposits on an industrial scale. It provides a good example of how the development of scientific knowledge radically alters previous ideas in course of time. In other words, the development of the history of the rare-earth elements led to the breakdown of the concept "rare" for 15 elements of Mendeleev's periodic system.

The reader will of course remember the name of the mineral from which "ceria" was isolated—cerite or ochroite, which got its name from the brownish-yellow colour which it acquired on heating. It turns out that this interesting mineral became well-known much earlier. As early as 1752 Cronsted had described it under the name of tungsten or "heavy stone", found in Sweden. After some time a similar mineral was found in Bohemia. Gadolinite, which initiated the yttrium group of



rare-earth elements, was described in detail by Geiger in 1788, i.e. shortly after Lieutenant Arrhenius's discovery.

It is worth noting that these minerals were subjected to analyses even before the researches of the discoverers of yttrium and cerium. Bergman and D'Elhuyar, two great chemists of their time, tried to determine the composition of the new minerals. Possibly the imperfect experimental technique, the undeveloped state of analytical chemistry still in its infancy, did not allow these investigators to discover yttria and ceria one or two decades earlier, for they wrongly took these "rare earths" to be lime.

Of course in the beginning the discovery of new minerals of "rare earths" was accidental in nature. But their number grew steadily though slowly. Fergusonite was discovered in 1806; two years later orthite was finally recognized as an independent mineral. In 1824 Berzelius discovered aeschynite in mineral specimens from the Urals, and in 1839 Scherrer analyzed the next rare-earth mineral—cuxenite.

Increasing interest in the chemistry of the "rare earths" gave rise to intensive research on their mineralogy also. Auer von Welsbach's use of cerium oxide in incandescent mantles made it necessary to look for large deposits of rare-earth minerals. It is worth noting that Welsbach himself played an important role in solving this problem by organizing a number of geological expeditions at his own expense. Large deposits of monazite, the most important rare-earth ore, were thus discovered.

If we now try to draw up a list of all the minerals in which the rare-earth elements are found, we shall have to spend many hours and fill up no less than 5–6 pages of this book. And no wonder, for the number of these minerals is nearing the impressive figure of 180.<sup>(15)</sup> But we shall not make such a count. Instead we shall give the reader the names of the principal minerals containing the rare-earth elements (Table 5).

Even a cursory glance at the table shows that the rare-earth elements enter into the constitution of minerals belonging to various groups—oxides (incidentally, most of the rare-earth minerals belong to this group), complex in their composition; halogen compounds, carbonates, phosphates and silicates. But

TABLE 5  
Principal minerals of the rare-earth elements

Mineral	Chemical nature of the mineral	Percentage of oxides of rare-earth elements	
		Elements of the cerium group	Elements of the yttrium group
Monazite	Isomorphous mixture of RE (rare-earth) phosphates with Th orthosilicate . . . .	42.3 – 66.9	0.5 – 4.8
Xenotime	RE orthophosphate . . . .	0.3 – 4.6	51.9 – 62.6
Bastnezite	Fluorocarbonate of rare-earth elements . . . .	73 – 76	—
Orthite (allanite)	Hydrated aluminium silicate of RE, Ca and Fe . .	13.4 – 27.4	0 – 2.2
Cerite	Hydrated RE silicate . . .	59.4 – 67.9	—
Yttrocerite	Hydrated fluoride of Ca and RE . . . . .	8.5 – 15.5	14.3 – 24.1
Gadolinite	Silicate of RE, Be and Fe .	2.9 – 7.9	30.9 – 46.6
Loparite	Titanoniobate of Ca, RE and alkali metals . . . .	30.7 – 34.1	0 – 0.5
Euxenite	RE titanoniobate . . . .	0.2 – 4.3	18.2 – 28.1
Fergusonite	Isomorphous mixture of niobotitanotantalates of RE and Fe . . . . .	0.9 – 6.2	31.2 – 42.3
Samarskite	RE Pyrotantaloniobate .	0.3 – 1.7	9.1 – 37.7

the main portion of the rare-earth elements on the earth's surface is concentrated not in these minerals which are rich in them, but in the abundant minerals of other elements, in which lanthanides occur as second-degree components. Calcium phosphate (apatite) should be mentioned as the most important of such minerals. From a study of a large number of specimens of apatites from different deposits I. D. Borneman-Starynkevich proved conclusively that phosphates of rare-earth elements constantly enter the composition of this mineral. Although their content is relatively low (from traces to 3.2 per cent) apatite is so abundant that this fact served as a justification at one time

for one of the founders of geochemistry, A. E. Fersman, to examine the content of the rare-earth elements.

We do not propose to consider in detail the nature of the abundance of the minerals containing the rare-earth elements or the forms in which they occur. But the main fact we wish to underline is that these elements belong to the lithophilic elements. Here we cannot avoid a short incursion into geochemistry.

Generally speaking, elements belonging to the lithophilic group are those that mainly form mineral ores. This is a very large group containing about 50 elements. Among them may be found such widespread elements like O, Si, Al, Ca, Mg, Na, etc.

Geochemists distinguished certain features characterizing lithophilic elements: (1) ions with an outer shell of 8 electrons,<sup>(16)</sup> which makes them highly active chemically and accounts for the absence of these elements in the free state in nature, (2) the presence of paramagnetism and (3) the maximum abundance of oxygen compounds.

The rare-earth elements possess all these features. Yttrium with an ion with charge three containing 2 electrons in the outer shell also has these features.

It will be recalled from the first chapter that the "rare earths" were for a long time considered to be oxides of bivalent elements. This seemed to be confirmed by the isomorphism of the rare-earth elements with the bivalent alkaline earths and chiefly with Ca. The latest geochemical investigations have shown that the isomorphism between the rare-earth elements ( $\text{Me}^{3+}$ ) and the usual trivalent elements (Al, Fe, etc.) is very weak, but at the same time is characteristic between  $\text{Me}^{3+}$  and bivalent strontium and calcium. Geochemical investigations serve to support Mendeleyev's bold decision to consider the rare-earth elements as trivalent.

The characteristic electronic structure of the rare-earth elements finds expression in the fact that they occur together in nature, in the same minerals. Besides the rare-earth elements, these minerals contain elements like Ca, Sr, Ti, Nb, Ta, Th, C, F, P, etc. At the same time a number of interesting characteristics may be noted in the case of the rare-earth elements.

The valency of the rare-earth elements in minerals is, as a rule, 3. But the presence of quadrivalent cerium and praseodymium has been observed in some natural compounds. The existence of  $\text{Eu}^{2+}$  has been shown in the case of europium. It is possible that this is the reason for the considerably lower (compared to the other rare-earth elements) content of europium in natural minerals. It thus seems to be distinct from  $\text{Me}^{3+}$ . An interesting confirmation of this fact is the discovery of isomorphism between  $\text{Eu}^{2+}$ , on the one hand, and strontium, barium, lead on the other.

From Table 5 it can be seen that different minerals contain different amounts of elements of the cerium and yttrium groups, sometimes one group predominating, sometimes the other.

Thus, for example, in monazite the cerium group plays the dominant role (42–67 per cent) while xenotime contains predominantly elements of the yttrium group (52–63 per cent).<sup>(17)</sup>

The investigation of the geochemical characteristics of rare-earth elements owes a great deal to many scientists, chiefly to geochemists like A. E. Fersman, V. I. Vernadskii, V. M. Gol'dschmidt and F. Clark.

Scientists had long been interested in the question of the amount of the different elements on the earth's surface. But for a long time they were forced to content themselves with a very rough and approximate estimate. Oxygen and silicon, for example, were considered to be the most abundant elements because of the very large variety of their compounds. For most of the other elements the estimates were extremely inaccurate, because elements like copper, lead, gold and silver which had long been used by man, were considered to be widely distributed. On the other hand, a whole series of elements were spoken of as being "rare" solely on the basis of external factors (absence of rich deposits, small relative content in minerals etc.). In fact, as the reader already knows, this was the fate of the rare-earth elements.

The first attempt to give a quantitative picture of the abundance of the elements on the earth's surface was due to the American geochemist Frank Clark. He worked out a method for calculating the average element composition of the earth's surface. Clark's data were supplemented and improved by

Gol'dshmidt, Vernadskii and Fersman. The latter introduced the concept of "Clarks of elements", numbers which express the mean content of chemical elements on the earth's surface in percentages by weight (in percentages of the weight of the earth's surface).

The curve of the abundance of the elements is given in Fig. 7. The values of  $Z$  are plotted along the abscissa, and the logarithms of the mean content of the elements along the ordinate. It can be seen from the curve that the abundance decreases with increase in  $Z$ . If the content of the most abundant element, oxygen, (49.13 per cent by weight) is compared with that of the rarest, protactinium, the ratio O : Pa will be expressed by

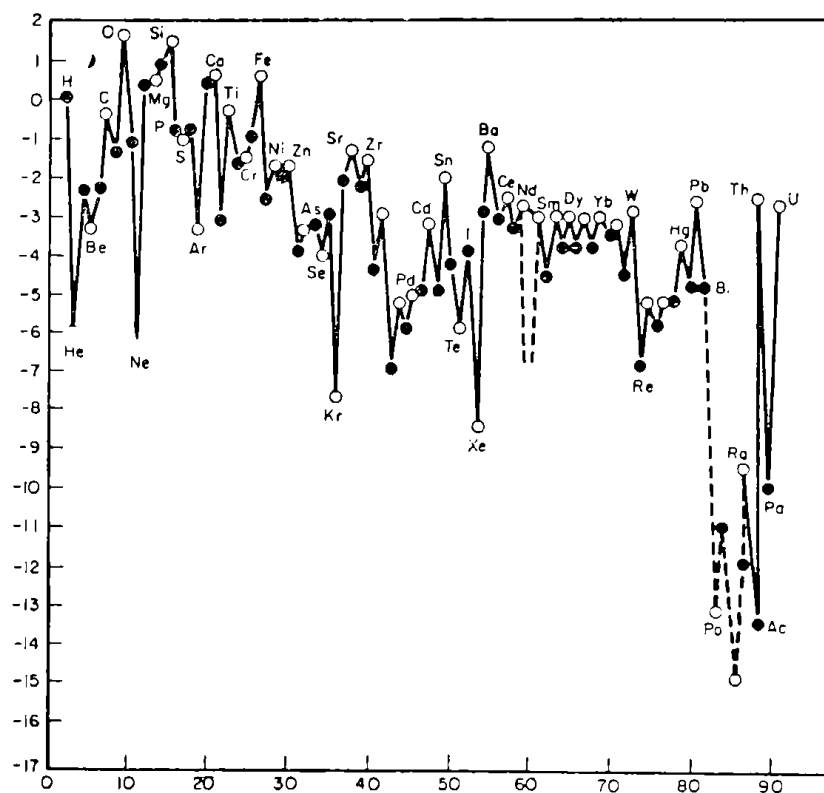


FIG. 7. Distribution curve of the elements.  
 Abscissa — nuclear charge ( $Z$ ); ordinate — logarithm of percentage by weight of the element in the earth's crust; O — even elements; ● — odd elements.

the astronomical figure  $10^{15}$ . Light elements (with small  $Z$ ) are the most abundant, 99.88 per cent by weight falling to their share (up to Fe,  $Z = 26$ ). Elements with even serial numbers

are, as a rule, more abundant than those with odd, the amount of the former exceeding that of the latter by more than six times.

Let us now turn to the position of the rare-earth elements on the curve of abundance. If the portions before and after them are separated, then for these portions (H–Ba and Hf–Pu) an extraordinarily wide divergence in the values of their abundance is found to be characteristic for these portions. In the section containing the rare-earth elements the curve has the appearance of a classic harmonic, the mean values not differing by more than one order.

Let us draw the curve of the abundance of the rare-earth elements separately (Fig. 8). The reader can now see a table giving the clarks of the rare-earth elements also (Table 6). An analysis of the data given in the table once again confirms the rule that even-numbered elements are relatively more abundant than their odd-numbered neighbours.

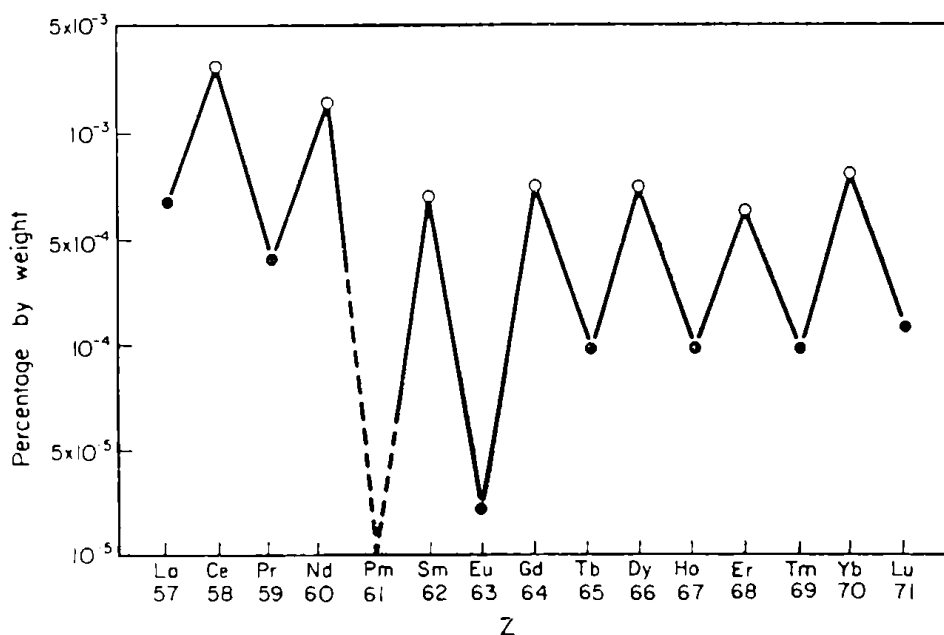


FIG. 8. Distribution curve of rare-earth elements.  
○ — even elements; ● — odd elements.

If the rare earth elements are arranged in the order of their abundance, according to A. E. Fersman's data, we shall get the following series:

Ce (Z=58)	Nd (Z=60)	Yb (Z=70)	Gd (Z=64)	Dy (Z=66)	Sm (Z=63)	63
$2.9 \times 10^{-3}$	$1.7 \times 10^{-3}$	$8 \times 10^{-4}$	$7.5 \times 10^{-4}$	$7.5 \times 10^{-4}$	$7 \times 10^{-4}$	
La (Z=57)	Er (Z=68)	Pr (Z=59)	Lu (Z=65)	Tb (Z=65)	Ho (Z=67)	4
$6.5 \times 10^{-4}$	$6.5 \times 10^{-4}$	$4.5 \times 10^{-4}$	$1.7 \times 10^{-4}$	$1 \times 10^{-4}$	$1 \times 10^{-4}$	
Tm (Z=69)	Eu (Z=63)					
$1 \times 10^{-4}$	$2 \times 10^{-5}$					

Thus the most abundant element is cerium and the least abundant europium. But if we proceed from the more recent and more accurate data of A. P. Vinogradov, we find that lanthanum and not ytterbium is the third most abundant element. Lutetium and thulium close the series. The values of the clarks of the rare-earth elements will, generally speaking, be revised more than once in future.

TABLE 6  
*Percentage of rare-earth elements in the earth's crust*

Serial Number	Symbol	Percentage by weight	
		According to A. E. Fersman	According to A. E. Vinogradov*
57	La	$6.5 \times 10^{-4}$	$1.8 \times 10^{-3}$
58	Ce	$2.9 \times 10^{-3}$	$4.5 \times 10^{-3}$
59	Pr	$4.5 \times 10^{-4}$	$7 \times 10^{-4}$
60	Nd	$1.7 \times 10^{-3}$	$2.5 \times 10^{-3}$
61	Pm	—	—
62	Sm	$7 \times 10^{-4}$	$7 \times 10^{-4}$
63	Eu	$2 \times 10^{-5}$	$1.2 \times 10^{-4}$
64	Gd	$7.5 \times 10^{-4}$	$1 \times 10^{-3}$
65	Tb	$1 \times 10^{-4}$	$1.5 \times 10^{-4}$
66	Dy	$7.5 \times 10^{-4}$	$4.5 \times 10^{-4}$
67	Ho	$1 \times 10^{-4}$	$1.3 \times 10^{-4}$
68	Er	$6.5 \times 10^{-4}$	$4 \times 10^{-4}$
69	Tm	$1 \times 10^{-4}$	$8 \times 10^{-5}$
70	Yb	$8 \times 10^{-4}$	$3 \times 10^{-4}$
71	Lu	$1.7 \times 10^{-4}$	$1 \times 10^{-4}$
39	Y	$5 \times 10^{-3}$	$2.8 \times 10^{-3}$

\*Not allowing for the percentage of rare-earth elements in the hydrosphere and atmosphere.

It would be wrong to try to find any regularities in the values of the abundance of the rare-earth elements on the basis of the electronic structures only, just as it would be wrong to look for such regularities proceeding from the distribution of the elements over the periods of Mendeleev's table. The values of the abundance of the elements are found to be closely related to the structure and the stability of atomic nuclei.

Now we have to show that the rare-earth elements are by no means rare. We can do this by a simple comparison of their clarks.

The sum of the clarks of the rare-earth elements (i.e. their total content on the earth's surface in per cent by weight) is  $1.6 \times 10^{-2}$  per cent (according to the data of A. P. Vinogradov).

Now we shall give the values of the clarks (in per cent) for some elements which have not been considered rare from ancient times and have been used by men:

silver— $1 \times 10^{-5}$	tin— $8 \times 10^{-3}$
antimony— $5 \times 10^{-5}$	platinum— $2 \times 10^{-5}$
lead— $1.6 \times 10^{-3}$	mercury— $5 \times 10^{-6}$
gold— $5 \times 10^{-7}$	

It can be seen from a comparison of these figures that the clark of the rare-earth elements is twice as large as that of tin, 10 times as large as that of lead, 320 times as large as that of antimony, 1600 times as large as that of silver, 2500 times as large as that of mercury and 32,000 times as large as that of gold.

If we take the rare-earth elements separately, we shall find that the abundance of any of them considerably exceed the amount of any of the "usual" elements (except tin) mentioned above on the earth's surface. Even such a rare-earth element like europium, for example, is more abundant on the earth's surface than silver, mercury and gold taken together! If the clarks of all the elements are written in a row, the rare-earth elements will occupy the 25th place in such a list.

The idea of lanthanides as rare elements thus breaks down completely.



## CHAPTER 3

# THE PROPERTIES OF THE RARE-EARTH ELEMENTS AND METHODS FOR THEIR SEPARATION

THE surprising similarity of the rare-earth elements among themselves is the main reason for the difficulty experienced in obtaining pure preparations of a single element. The production of metals of a high degree of purity is a very complicated task since it depends greatly on the purity of the initial preparation. Moreover, the product obtained is easily contaminated with impurities (the reducing agent, the material of the apparatus) and requires further purification.

While most of the elements of the cerium group were isolated in a reasonably pure state by the end of the 19th and the beginning of the 20th centuries and their properties studied by chemists in sufficient detail, the yttrium group of the rare-earth elements present a different picture.

In actual fact, they were obtained in the form of metals only in the last 15–20 years. Naturally data on their properties is still far from complete.

The values of many constants (melting and boiling points, density, electrical conductivity) often differ greatly in the literature on the rare-earth elements. This, evidently, is to be explained by the fact that different investigators were dealing with specimens of different degrees of purity. For this reason we are compelled in many cases to give not a definite value for a certain constant but the interval between the extreme values.

### 1. The Physical and Chemical Properties of the Rare-earth Elements

The physical description of metals begins, as a rule, with a description of their external appearance. In the free state the rare-earth elements are lustrous metals, their lustre reminding

one of metallic iron or silver with tinges varying from chestnut to dark brown.

Generally speaking, the colour of the smooth surface of a particular rare-earth metal depends on the presence of impurities as well as on the formation of a film of oxide (or nitride) on the surface.

The density of the rare-earth elements increases regularly with atomic number, i.e. along the La–Lu series. Exceptions to this rule are the anomalous densities of europium and ytterbium, a fact explained by the crystal lattices in these elements (see Table 7).

TABLE 7  
*Density of rare-earth elements, g/cm<sup>3</sup>*

Symbol	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd
Density	6.162	6.768	6.769	7.007	(7.260)	7.540	5.166	7.868
Symbol	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
Density	8.253	8.565	8.799	9.058	9.318	6.959	9.849	4.472

A similar general variation—increase with increasing serial number—is found for the melting points of the rare-earth elements also. Anomalous values in this case are found for cerium, europium and ytterbium. On the whole, rare-earth metals are very difficult to melt. Their boiling points are very high and are lowest at europium and ytterbium. The data are summarized in Table 8.

The distribution of the melting points on the curve of the melting points for all the elements of the periodic system is interesting. In each period, in general an increase in the values is observed for the first half of the period and a sharp drop for the second (as is seen particularly clearly in the second and the third periods), in the section La–Lu, i.e. over 15 elements, there is a smooth and relatively small rise in the melting points. This is a consequence of the slight increase of atomic radii in the series of rare-earth elements (Fig. 9).

TABLE 8  
*Melting and boiling points of rare-earth metals*

Symbol	m.p.	b.p.	Symbol	m.p.	b.p.
La	920 $\pm$ 5	4515	Tb	1400 – 1500	2800
Ce	804 $\pm$ 5	3600	Dy	1475 – 1500	2600
Pr	935 $\pm$ 5	3450	Ho	1475 – 1525	2700
Nd	1024 $\pm$ 5	3300	Er	1475 – 1525	2600
Pm	(1035 $\pm$ 10)	?	Tm	1500 – 1550	2400
Sm	1052 $\pm$ 5	1900	Yb	824 $\pm$ 5	1800
Eu	900	1700	Lu	1650 – 1750	3500
Gd	1350 $\pm$ 20	3000	Y	1475 – 1525	3500

The mechanical properties of the rare-earth elements have not been studied adequately.\* It is known however that they are not very hard and that the hardness increases slightly along the series La–Lu. A fair malleability is characteristic of the metals, ytterbium and, apparently, europium, being the most malleable because of their relative softness. It should be mentioned that the hardness and malleability of the lanthanides depend considerably on the methods of their preparation and treatment.

An intensive study is being made of the electrical and magnetic properties of the rare-earth elements. On the whole (although this can be said definitely for elements of the cerium group only), the rare-earth elements are very poor conductors of electricity. Their electrical conductivity is of the order of  $10^{-8}$  ohms. It has been discovered recently that at temperatures close to absolute zero, lanthanum becomes a super-conductor.

A number of scientists have investigated the super-conductivity of the lanthanides, but concrete results have not yet been obtained.

The magnetic properties of the rare-earth elements are very curious and interesting. As is well-known, ions of all elements of the periodic system are magneto-active to some extent. This is explained by the magnetic properties of the nuclei and the

\*Yet see Love: WADC Technical Report 57-666.

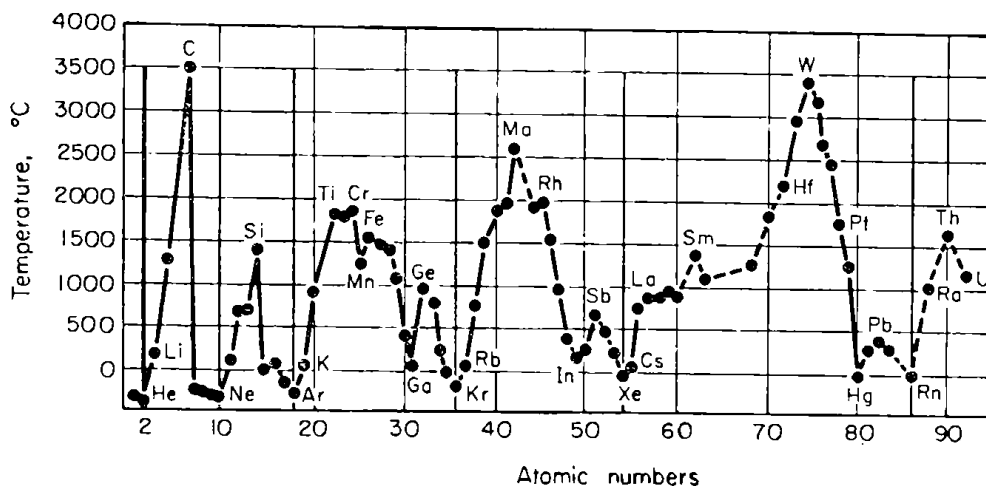


FIG. 9. Curve of melting points of the elements.

electrons, the constituents of the atoms. The magnetic susceptibility ( $\kappa$ ) serves to characterize quantitatively the magnetic properties; substances with a positive value of  $\kappa$  are called paramagnetic.

The rare-earth elements and their compounds are strongly paramagnetic.\* They have very high values of  $\kappa$ . In this case a special role is played by the incomplete magneto-active  $4f$ -subshell which is protected by the closed outer shells  $5s$  and  $5p$  from the influence of extraneous fields. The values of the magnetic susceptibility for the rare-earth elements are given in Table 9.

TABLE 9  
*Magnetic susceptibility of rare-earth elements at room temperature*

Symbol	La	Ce	Nd	Eu	Gd	Tb	Er	Tm	Yb	Y
$\kappa \times 10^6$	140	2300	3600	30 400	75 000	113000	44 500	25 600	250	191

For purposes of comparison we may note that the values of  $\kappa$  for a number of well-known paramagnetic metals are not high.

\*Scandium, yttrium, lanthanum and lutetium are not paramagnetic, but in fact somewhat diamagnetic.

Thus, for example, for Mg it is 6, for Be 20, for Ti 150, for Cr 160 etc. (in the same units).

If the variation in the magnetic properties of the rare-earth elements is depicted graphically, the curve obtained (Fig. 10) will have two maxima. More accurately, it consists of two separate curves, corresponding in general to elements of the cerium and yttrium groups respectively.

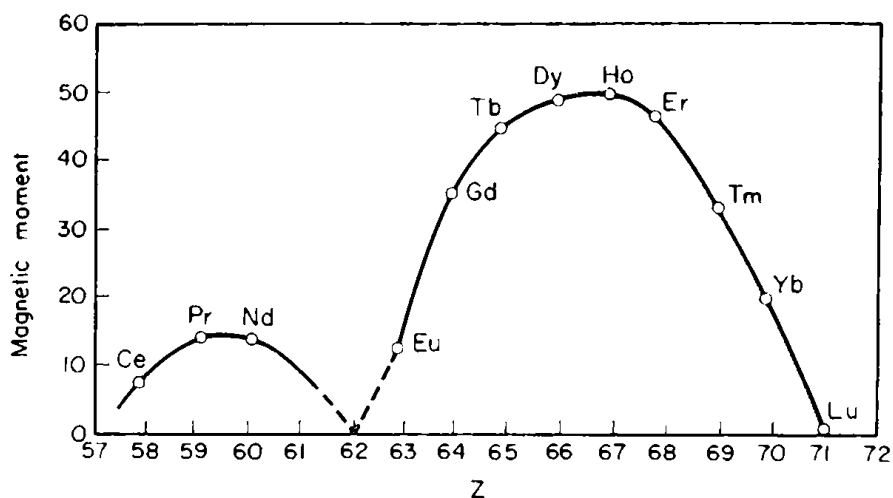


FIG. 10. Curve of the magnetic susceptibility of rare-earth elements.

Thus the nature of the variation of the paramagnetic properties in the series of rare-earth elements is, as it were, an additional experimental confirmation of the division of the family into two groups.

It is not without reason that we have pointed out in the heading of Table 9 that the values of  $\chi$  given correspond to room temperature. The fact is that the magnetic properties of the rare-earth elements change with change in temperature. An exception is perhaps formed by cerium, which retains its paramagnetism even in liquid nitrogen. The elements of the yttrium group, beginning with dysprosium, become ferro-magnetic<sup>\*(18)</sup>.

Let us now pass on to the chemical characteristics of the rare-earth elements. We have already emphasized repeatedly the surprising chemical resemblance among these elements. But

\*This is not the case with scandium, yttrium, lanthanum or lutetium.

for all their similarity certain differences also stand out quite distinctly.

The rare-earth elements are quite stable with respect to dry air. Only lanthanum loses its lustre after some time. In moist air however, surface deterioration commences quite rapidly in all the pure lanthanide metals. On heating to 200–400°C the metals ignite (the first few members of the family do so very easily) and burn with the formation of oxides. As for cerium, in the powdery state it is pyrophoric, i.e. it catches fire by itself in air. It is interesting to note that in pure oxygen, compact metallic cerium catches fire at a lower temperature than aluminium or magnesium.

If the variation in the rate of oxidation over the entire series of the rare-earth elements is observed, the following picture will emerge. Lanthanum and cerium are strongly oxidized; praseodymium and neodymium (well-cleaned) are subject to oxidation to a considerably smaller extent. Pure gadolinium remains unaffected in air for many months. The oxidizability increases in the first few elements of the yttrium group, but decreases again towards the end.

As the rare-earth metals are chemically very active, they react easily with many non-metals.

At high temperatures nitrides of the rare-earth elements with the general formula  $MeN$  are formed with nitrogen. Nitrides can also be obtained by calcining a mixture of a metallic powder and  $KCl$  (in the ratio 1:3) in a corundum boat in a current of  $NH_3$  at 700°C.

Rare-earth elements actively combine with sulphur. Some lanthanides form sulphides with different compositions. Cerium, for example, gives the compounds  $Ce_2S_3$ ,  $Ce_3S_4$  and  $CeS$ . Among metallic sulphides these substances are the most difficult to melt. Their melting point is higher than 2000°C. Aluminium oxide and metallic titanium, which are different to melt, can be melted in cerium sulphide— $CeS$  (m.p. 2450°C).

The rare-earth metals combine with the halogens to form the corresponding halides.

They interact easily with carbon, silicon, arsenic and phosphorus, forming compounds of definite compositions.

The existence of hydrides of the type  $\text{MeH}_2$  and  $\text{MeH}_3$  can be considered as proved now for La, Ce, Pr, Nd, Sm and Gd. Many researches on the preparation of hydrides of Eu and Yb also have been carried out and in a number of cases their composition has been established.

Among alloys of the rare-earth elements with other metals, studies have been made chiefly of the alloys of the elements of the yttrium group. Alloys with Na, Cu, Ag, Au, Ca, Mg, Zn, Al, Hg etc. are known in particular.

All the rare-earth metals without exception have a low resistance to acids. Sulphuric and hydrochloric acids of any concentration, and also concentrated nitric acid, dissolve these metals easily. Dilute nitric acid however acts only on metallic cerium.

The rare-earth elements are rather inert with respect to the alkalis. But the chlorides of the alkali metals exert a certain dissolving action. Since they are strong reducing agents, the rare-earth elements are capable of expelling hydrogen from water. The process is more intense in hot water.

The compounds of the rare-earth elements with oxygen are the ones that are the most interesting and important.

The oxides, which in fact were originally known as "rare earths", have played a very important role in the development of the chemistry of the rare-earth elements.

The oxides of the trivalent rare-earth elements have the common formula  $\text{Me}_2\text{O}_3$ . For cerium the dioxide  $\text{CeO}_2$ , in which the metal is quadrivalent, is also characteristic.

The oxides may be obtained by the direct interaction of the rare-earth metals with oxygen. Considerable amounts of heat are liberated in the process, as in the formation of the oxides of the alkaline earth metals. Thus the heat of formation of  $\text{La}_2\text{O}_3$  (in kcal/mol) is 214,  $\text{CeO}_2$  260,  $\text{Nd}_2\text{O}_3$  216 and  $\text{Gd}_2\text{O}_3$  217. Another method of preparing the oxides of the rare-earth elements consists in calcining their hydroxides or oxy-anion salts—carbonates, oxalates, nitrates; the reaction does not proceed smoothly, it is true, in the case of the salts of cerium, praseodymium and terbium. The oxides of the rare-earth elements are very difficult to melt; cerium oxide, for example, melts at a temperature of about  $2500^\circ$ .

The colours of the rare-earth oxides vary considerably\*. Thus the oxides of La,  $\text{Ce}^{3+}$ , Yb and Lu are colourless. A pink-red shade is characteristic of  $\text{Er}_2\text{O}_3$ ,  $\text{Tb}_2\text{O}_3$  and to a very small degree for  $\text{Eu}_2\text{O}_3$ . The oxides of samarium, dysprosium and holmium are distinguished by a yellow colour. The colouring is most distinct in the case of  $\text{Pr}_2\text{O}_3$ —a green colour—and in the case of  $\text{Nd}_2\text{O}_3$ —blue. A reddish yellow colour is characteristic of cerium dioxide.

Incidentally, in the early stages of the development of the chemistry of the “rare earths” one of the qualitative methods for the identification of the different elements was the colour of their oxides and salts.

A strongly marked basic character is typical of the oxides of the rare-earth elements. This becomes weaker along the series La–Lu. As a result of this, there is no interaction with alkalis.† The solubility of  $\text{Me}_2\text{O}_3$  in acids depends to a considerable extent on the method of preparation of the oxide and the temperature of calcination. But other conditions remaining equal, the rate of dissolution drops noticeably with increase in the serial number.

The oxides do not dissolve in water but can combine with it to form hydrates of the oxides.

Of no less interest are those oxides in which the anomalous valencies of the rare-earth elements appear. Among these the one most studied and also most important in practice is cerium dioxide  $\text{CeO}_2$ .

It can be prepared by the calcination of either the metal itself or its oxy-anion salts.  $\text{CeO}_2$  is so stable that hydrogen reduces it with difficulty except at very high temperatures (of the order of  $2000^\circ$ ) and at a pressure of 150 atm.

\*Many workers will not agree with the immediately following statements. Colours of rare-earth oxides are grossly affected by small amounts of impurity. Pure (99.99 per cent)  $\text{Tb}_2\text{O}_3$  and  $\text{Eu}_2\text{O}_3$  are white with no pink colouring; it is probable that any yellow tinge in dysprosium and holmium oxides is attributable to traces of terbium in its higher valence state. Cerium oxide has no reddish tinge to it—this is imparted by praseodymium—and when pure the oxide has only a slightly off-white tint.

†Some solubility of ytterbium and lutetium has been observed in alkaline solutions—scandium is notably amphoteric.



The basic properties of  $\text{CeO}_2$  are expressed much more weakly than in the case of the oxides of the trivalent elements. This is demonstrated clearly by its relative insolubility in hydrochloric or nitric acid, a fact which played a part in Mosander's separation of lanthanum from "ceria".

$\text{CeO}_2$  is the only oxide of the rare-earth elements with an anomalous valency which gives rise to a whole series of compounds of  $\text{Ce}^{4+}$ .

Due to the weak basicity of  $\text{CeO}_2$ , the salts of  $\text{Ce}^{4+}$  are strongly hydrolysed in solution. In an acidic medium  $\text{Ce}^{4+}$  is a very strong oxidizing agent.

The quadrivalent state is also observed in praseodymium and terbium.

The valence states of praseodymium were a controversial matter for a number of years. It is recognized nowadays that the highest oxide of praseodymium corresponds to the formula  $\text{PrO}_2$ ; praseodymium dioxide can be obtained by the oxidation of the sesqui-oxide with  $\text{KClO}_3$ . When salts of  $\text{Pr}^{3+}$  are calcined in air however, an intermediate product is formed, the composition of which corresponds to  $\text{Pr}_6\text{O}_{11}$ . It was suggested that this compound should be considered as  $\text{Pr}_2\text{O}_5 \cdot 2\text{Pr}_2\text{O}_3$ , i.e. praseodymium should be considered as having a pentavalent state. But no proof of the existence of  $\text{Pr}^{5+}$  was obtained, and probably  $\text{Pr}_6\text{O}_{11}$  should be considered as  $\text{Pr}_2\text{O}_3 \cdot 4\text{PrO}_2$ . All the same it should be noted that, from general considerations (the ion  $\text{Pr}^{5+}$  has the stable configuration of xenon) a pentavalent state is possible for praseodymium.

Terbium presents a similar picture. In this case however, the composition of the intermediate compound corresponds to the formula  $\text{Tb}_4\text{O}_7$ , or  $\text{Tb}_2\text{O}_3 \cdot 2\text{TbO}_2$ .

Hydrogen reduces the higher oxides of praseodymium and terbium considerably more easily than  $\text{CeO}_2$ .

Moreover, as distinct from  $\text{Ce}^{4+}$  neither praseodymium nor terbium gives ions with a charge 4 in solution.

Due to the insolubility of the oxides of the rare-earth elements in water, their hydroxides can be obtained only in an indirect manner, e.g. by the addition of alkalis to solutions of the salts of the lanthanides.

The general formula of the hydroxides of the rare-earth

elements is  $\text{Me}(\text{OH})_3$ , but with the help of X-rays it was possible to demonstrate the existence of hydroxides of the type  $\text{MeOOH}$ , a specific intermediate compound between  $\text{Me}(\text{OH})_3$  and  $\text{Me}_2\text{O}_3$ .

It is interesting to note that the salts of alkali metals formed from some organic acids (citric, tartaric), sugar, ammonium acetate, etc., interfere with the precipitation of the hydroxides of the rare-earth elements. This fact played an important part in the study of the processes of complex-formation in rare-earth elements (see below).

When speaking of the oxides of the rare-earth elements we mentioned that their basicity drops over the series La–Lu. There is a similar picture in the case of the hydroxides also. This drop in basicity can be explained as follows.

Let us think of the hydroxide of a rare-earth element in the form of the scheme given in Fig. 11. The shaded circle in the

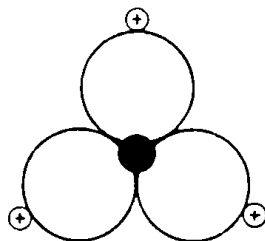


FIG. 11. Schematic representation of the hydroxide of rare-earth elements.

centre is the ion  $\text{Me}^{3+}$ ; the large circles are the oxygen ions; the small white circles with the plus sign (+) inside are hydrogen ions. Between the  $\text{Me}^{3+}$  ion and the oxygen ion on the one hand, and the  $\text{H}^+$  ion and the oxygen ion on the other, there are certain forces of attraction due to the opposite signs of the charges. In our case the only variable quantity is the size of the  $\text{Me}^{3+}$  ion. This size decreases over the La–Lu series because of the lanthanide contraction. But as a result of the decrease in the radius of  $\text{Me}^{3+}$  its forces of attraction with the oxygen ion increase while the O–H bond remains as before. It is true that even in lutetium the O–H bond remains more stable than the Me–O bond and acid dissociation (i.e. with the release of  $\text{H}^+$ ) is not observed in the hydrate of lutetium oxide. Basic dissociation (i.e. with the release of  $3\text{OH}^-$ ) becomes weaker as  $Z$  increases

from lanthanum to lutetium i.e. as the basic properties of their hydroxides become weaker.

All the hydroxides of the rare-earth elements are relatively insoluble in water. Their solubility decreases from lanthanum to lutetium.

This is the reason why the hydroxides do not give a high concentration of  $\text{OH}^-$  ions in solution although the rare-earth metals are strongly basic. The solubility product—a quantitative expression for the solubility of difficultly soluble compounds—is given by the product of the concentrations of the ions of a given compound in a saturated solution,  $[\text{Me}_3^+][\text{OH}^-]^3$ . This has been estimated as  $10^{-19}$  for  $\text{La}(\text{OH})_3$ ; as  $10^{-20}$  for  $\text{Ce}(\text{OH})_3$  and  $\text{Pr}(\text{OH})_3$ ; it goes down further, reaching  $10^{-24}$  for lutetium.

The rare-earth elements form a large number of salts with inorganic as well as organic anions.

The halides, nitrates, sulphates and oxalates, as also the binary salts of the rare-earth elements have been carefully studied. The difference in the solubility of many of these salts is used for the separation of the rare-earth metals from accompanying metals and also for the division of the family into its different parts.

## 2. From the Mineral to the Pure Metals

The separation of the rare-earth elements and the preparation of individual metals of a high degree of purity is a very difficult problem which has not been completely solved even today. Several methods of separating the rare-earth family into the different elements are known to contemporary chemistry but not one of these methods can be said to be universal, i.e., ensuring quick and sufficiently complete separation of all the individual elements.

We shall not consider in detail all the methods used—this is a subject for a larger and more comprehensive book, since the history of the chemistry of the rare-earth elements is to a considerable extent a history of the methods of their separation. We shall speak of them briefly.

A few examples will convince the reader of the complexity of the problem of separation of the rare-earth elements.

The double nitrate of praseodymium and magnesium had to be recrystallized about 5000 times to obtain praseodymium of 99 per cent purity by the method of fractional crystallization. Eight months of intense work were required for the purpose. The separation of 99 per cent thulium was even more laborious: a 20 per cent concentrate was obtained after 6 years of work. Another 4 years were required for separating pure thulium by recrystallization of its bromates.

And finally, pure holmium was obtained after 4 years of continuous work.

We have named the two oldest classical methods for the separation of the rare-earth elements—fractional crystallization and fractional basic precipitation. But before describing them briefly let us return to the question of differences in the properties of the rare-earth elements. For in the final analysis, the separation of any element from another is based on the difference in their properties.

The curiosity of scientists led them, even in the early stages of the development of the chemistry of rare-earth elements, to look for differences in the properties of the different metals and their compounds which would enable their separation as completely as possible. And such differences were found.

It was found that the salts of the rare-earth elements differ somewhat in their solubility in water. These small differences were used for separating a mixture of rare-earth elements into its components. Another method of separation was based on the decrease in the basicity of the hydroxides from La to Lu in the series.

These methods could not satisfy the present-day requirements of speed and completeness of separation. New methods were worked out: those based on the anomalous valencies of the rare-earth elements; ion-exchange chromatography; extraction with organic solvents.

But the old methods were not discarded. Here are some of them.

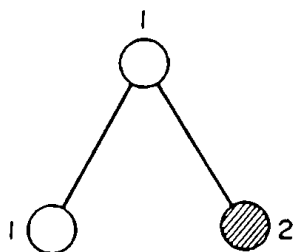
The method of fractional crystallization is based on differences in the solubility of compounds of the rare-earth elements. It is simple to carry out but very laborious and requires great care during the operations. The main drawback of the method is the

long duration of the work (extending to a number of years sometimes) due to the necessity of carrying out many thousands of operations of the same type.

The process of separation may be represented as follows.

A solution of the salts of the rare-earth elements is prepared. It is first freed of cerium by making use of the element's capacity to pass over easily to the quadrivalent state. The solution is evaporated until a sample drop crystallizes on cooling. The mass of the solution is then left overnight for slow crystallization. As a result the most soluble salts remain in the solution, while the least soluble precipitate out.

Let us depict this process schematically.



The shaded circle denotes crystals and the unshaded ones the solution. The figures denote the number of the fraction. From the initial fraction we obtained 2—the crystal and the solution, called the mother liquor.

The solution is separated from the crystals, evaporated again and left for crystallization. The crystals are dissolved and this solution is also evaporated. Thus, as a result of the second series of experiments two portions of crystals and two mother liquors are obtained. Next, both the mother liquors are poured off. The solution of the first fraction of the second series of experiments now forms the starting point of the third series of experiments. The mother liquor of the second fraction of the second series is added to the crystals of the first fraction of the same series. This process, the addition of crystals of one fraction to the mother liquor of the next fraction, in fact constitutes the essence of the method of fractional distillation. “The tree of crystallization” keeps on growing (see Fig. 12).

From Fig. 12 it can be seen that the lines on which the unshaded circles (the most soluble fractions) are situated and the

lines with the dark circles have different directions. Fractions of intermediate solubility will lie in the central part of the pattern.

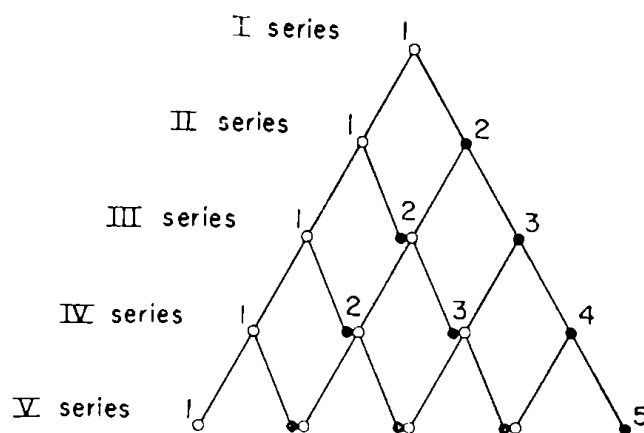


FIG. 12. Scheme of the fractional crystallization method.

While carrying out fractional crystallization it is necessary to check the purity of the fractions obtained. Physical methods of analysis come to one's aid here; the study of the absorption spectra of coloured salts, their emission spectra—right up to the methods of X-ray analysis.

Many scientists, among whom Mendeleev occupies an eminent position, have contributed to the development of the method of fractional crystallization. As early as 1873 he suggested the use of the very promising process of crystallization of double nitrates of ammonium and the rare-earth elements and used it in practice for separating lanthanum from didymium.

The compounds used for the separation of the rare-earth elements by the method of fractional crystallization are extremely varied: simple and double sulphates and nitrates, bromates, phosphates, chromates, iodates and a whole series of organic derivatives like acetyl acetonates, dimethyl phosphates, etc. It has been established that binary compounds, for example double sulphates of potassium and the rare-earth elements of the type  $\text{Me}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ , where Me is a rare-earth element, play a very important role. It is interesting to note that 3 concentrates can be separated by utilizing their varying solubility in an excess of the precipitating agent. These concentrates are enriched in the following elements respectively:

(1) La, Ce, Pr, Nd, Sm (form difficultly soluble double salts), (2) Gd, Tb and Eu (give slightly soluble salts) and lastly, (3) Dy, Ho, Er, Tm, Yb and Lu (the double salts are distinguished by their good solubility). This fact was used at one time for subdividing the "rare earths" into the cerium, terbium and yttrium groups respectively. This division was used by practical chemists for quite a long time.

The methods of fractional basic precipitation is perhaps the oldest method for the separation of elements. Berzelius used it for separating the cerium and yttrium earths. The method consists essentially in utilizing the different basicities of the hydroxides; the basicity diminishing with increase in  $Z$ , i.e., from lanthanum to lutetium. Ammonia, ammonium hydroxide, urea and some organic bases can be used as precipitating agents.<sup>(19)</sup>

Methods of separating the rare-earth elements, based on the different thermal stabilities of their compounds, have also been used for a long time, but they were found most useful for removing impurities of other compounds from the salts of the rare-earth elements. Nevertheless it should be mentioned that as a method its application for separating a mixture of rare-earth elements into its components is very laborious and time-consuming. An exception occurs only in the case of cerium, which can be isolated comparatively easily because of its ability to pass into the quadrivalent state on heating.

The new methods of separating the rare-earth elements are far more attractive. The chemistry of the rare-earth elements was still in its infancy when cerium was isolated in the quadrivalent state from a mixture of trivalent rare-earth elements. This was demonstrated by Vauquelin and Berzelius. It was by converting  $Ce^{3+}$  to  $Ce^{4+}$  that Mosander, who discovered several of the rare earths, was able to separate lanthanum with the help of further experiments. Even today the first step in the treatment of a mixture of rare-earth elements is the separation of  $Ce^{4+}$ .

As is well-known, in addition to cerium, terbium and praseodymium ( $Tb^{4+}$ ,  $Pr^{4+}$ ), samarium, europium and ytterbium ( $Sm^{2+}$ ,  $Eu^{2+}$  and  $Yb^{2+}$ ) also possess anomalous valencies. In these states the properties of the elements are different from

those of trivalent elements. It is this which makes it possible in principle to separate them.

The method of separating bivalent rare-earth elements had been known for a long time, but it was only in the last decade that it gained recognition. A number of methods are known for utilizing the valency state  $2+$  for the separation of Sm, Eu and Yb. One of these consists in the preparation of amalgams of the reduced lanthanide.<sup>(20)</sup>

An interesting field in which the  $Me^{2+}$  state is used for the isolation of Sm, Eu and Yb involves the reduction of a mixture of chlorides of the rare-earth elements by metallic calcium under suitable conditions. In this case an alloy is obtained which does not contain lanthanides capable of exhibiting the valency  $2+$ . These lanthanides pass into the slag.

The relative ease with which  $Ce^{4+}$  separates from the other rare-earth elements naturally suggested the idea of utilizing the capacity of praseodymium and terbium to pass into the valency state  $4+$ . But both these tasks—the preparation of the higher oxides of terbium and praseodymium with a sufficiently high yield, and their separation from the sesquioxides of other rare-earth elements—proved to be difficult. The method of solving these problems was found in the studies on the structures of sesquioxides of the rare-earth elements. It was found, in particular, that praseodymium oxide cannot be converted into the dioxide under the usual conditions. But heating to  $500^\circ$  brings about a re-arrangement of the structure, as a result of which  $Pr_2O_3$  becomes oxidized by oxygen into stable  $PrO_2$ .

The study of the dissolution of hydrated oxides of trivalent lanthanides in molten alkalis showed that they dissolve well in them at  $300$ – $320^\circ C$ .  $Pr_2O_3$  and  $Tb_2O_3$  can be oxidized to the quadrivalent state by raising the temperature. In this state they hardly dissolve and so can be separated.

A new feature in the chemistry of the rare-earth elements was constituted by a thorough study of their complex compounds. On the one hand, this helped to extend our knowledge of these elements and their compounds; on the other, it provided a theoretical basis for the separation of these elements with the help of ion-exchange chromatography. An important role was played in these investigations by the Soviet scientists D. I.



Ryabchikov and E. A. Terent'yeva. These scientists observed a very strong capacity in the rare-earth elements for complex-formation, especially with organic acids rich in oxygen (e.g. polybasic oxy-acids) and also organic compounds containing nitrogen. They were able to obtain complexes with organic amines, citric, tartaric, lactic and ethylene-diamine-tetraacetic acids and other compounds. It was shown that the stability of complexes in the series of rare-earth elements increases with the serial number, i.e., from La to Lu.

The usual view of the process of fractional crystallization as a method based on the different solubilities of the binary salts underwent a change in the light of Ryabchikov and Terent'yeva's investigations. To all appearances, the principal role here is played by the different stabilities of the complex compounds and the double sulphates, carbonates, formates etc. can be regarded as such. From these researches, as well as from those of other scientists, it was found that it was possible to obtain the individual components in the pure state under certain conditions and repeated separations. This is attributable to the different stabilities of the complex compounds of the rare-earth elements.

Extensive use of the complex compounds of these elements was made for separating the latter by the method of ion-exchange chromatography. In practice this is done as follows.<sup>(21)</sup>

Special chromatographic columns are filled with small heads of an ion-exchange resin—a cationite. Then, a solution containing ions of the rare-earth elements is passed through the column. In the upper part of the column they are absorbed by the heads of the cationite. Next, a so-called eluting solution of a complex-forming substance, e.g., citric or lactic acid, is passed through the column. This substance forms complexes of varying stability with the rare-earth elements. The cations begin moving down the column and the weaker the complex the slower is its cation washed out. For this reason, in the process of elution the cations of the different rare-earth elements are distributed at different points of the column. They come out of it in a definite sequence and can be collected in the form of separate fractions. The first to come out of the column should be the fraction containing lutetium, the last that of lanthanum.

The process of chromatographic separation can be represented graphically by curves of elution. These curves are given for a number of rare-earth elements in Fig. 13.

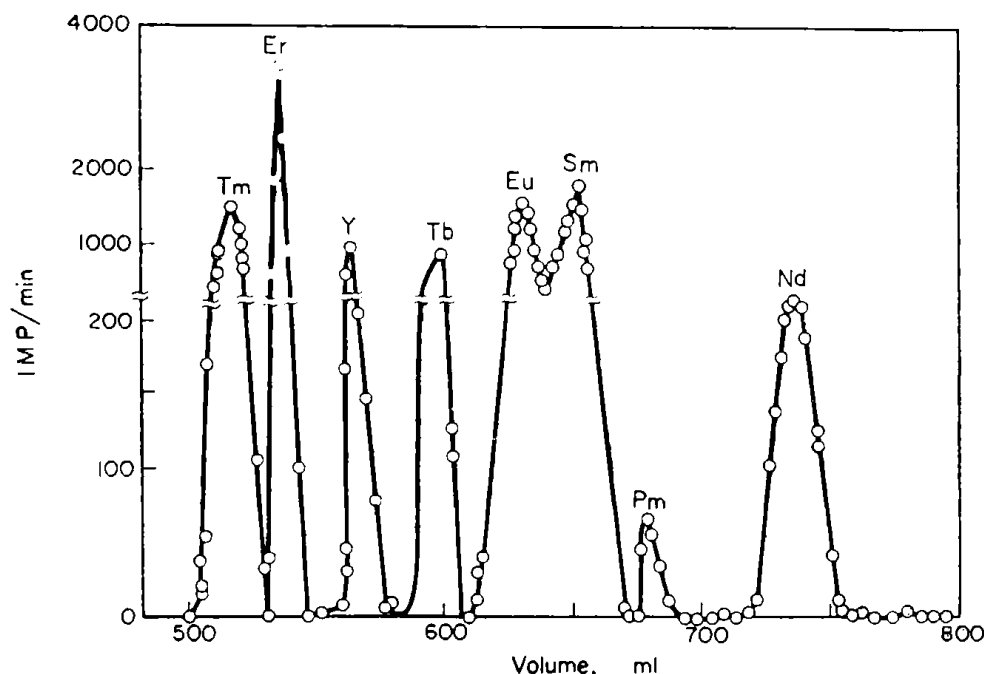


FIG. 13. Elution curves in the separation of rare-earth elements by ion-exchange chromatography.

The different members of the rare-earth family can be obtained in a very pure form by the method of ion-exchange chromatography. But a serious drawback of the method is its comparatively low yield, so that it is unsuitable for the treatment of large quantities of material.

From this short survey of the methods of separation of the rare-earth elements it can be seen that not one of them is completely efficient for obtaining any preparation of a rare-earth element in the pure state with sufficiently complete separation. The most economical way therefore is to combine the different methods, using different ones for the different stages of separation. The nature of the raw material and the contents of the cerium and yttrium groups should also be taken into account for the purpose.

The process of obtaining the rare-earth elements begins with the treatment of the raw material at the chemist's disposal in a particular case. The nature of the mineral determines the

method of decomposing the raw material, or to use the language of mineralogists, the method of "dissecting" the mineral. Thus, for example, hydrochloric acid is used for dissecting orthite or gadolinite (silicates of the rare-earth elements Monazite and xenotime (phosphates) are treated with concentrated sulphuric acid. Niobotantalates (fergusonite, euxenite, etc.) are decomposed with hydrofluoric acid or by fusion with a bisulphate. Chlorination is used in some cases.

The separation of the rare-earth elements from the elements accompanying them is not a complicated problem. They are precipitated from solutions by means of oxalic or hydrofluoric acid, ammonia or alkalies, i.e. by reagents forming difficultly soluble compounds with the rare-earth elements.

Further treatment of a mixture of rare-earth elements depends on whether the cerium or yttrium group predominates in the initial mineral. A third case is possible in which the two groups are present in roughly the same amounts (the so-called complete composition minerals).

It is highly desirable, of course, to have a preliminary division of the family of rare-earth elements, even if it is rough and incomplete. For minerals of complete composition it is convenient to remove cerium, thus reducing the amount of material belonging to the cerium group, and then carry out the division into groups using the different solubilities of the double sulphates. The same sequence of operations is to be recommended for the cerium containing raw material also, but before separating the sulphates it is necessary to carry out a rough crystallization separation of the cerium group.

In broad outline, the schemes of treatment of the cerium and yttrium raw material (after division into groups) will be as follows:

1. Scheme of treatment of the cerium raw material:
  - (a) Removal of Ce and La, as the most abundant rare-earth elements of the cerium group
  - (b) Concentration of Sm and Eu for electro-chemical separation
  - (c) Removal of Sm and Eu
  - (d) Separation of Nd and Pr

## 2. Scheme of treatment of the yttrium raw material:

- (a) Separation of yttrium
- (b) Electro-chemical separation of Yb
- (c) Separation of the remaining elements of the yttrium group by the method of ion-exchange chromatography

Radioactive isotopes of the rare-earth elements may be used for observing the process of separation.  $\text{La}^{140}$  in particular, is used for observing the separation of La; the indicators in the process of the electro-chemical separation of samarium and ytterbium are  $\text{Sm}^{153}$  and  $\text{Yb}^{175}$ .

Compounds of rare-earth elements (usually oxides or chlorides) of a more or less high degree of purity are obtained by means of lengthy and laborious processes. But it is by no means a simple task to obtain these elements in the metallic state.

The electro-chemical method is the oldest one for obtaining rare-earth metals in a sufficiently pure state. Lanthanum and some light lanthanides were obtained by this method as early as the end of the 19th century. With the help of the process of electrolysis of aqueous solutions it was possible to prepare an amalgam of the rare-earth elements if a mercury cathode was used. Another method involved the electrolysis of fused salts, usually chlorides. But in this case the material of the electrodes and the vessel in which electrolysis was carried out affected the purity of the metals obtained. Hillebrand and Norton, who were the first to use the electro-chemical method for obtaining the rare-earth metals, used a porcelain crucible and platinum electrodes. The final products were contaminated with porcelain and platinum. Muthmann, who during the years 1902–1907 obtained all the metals of the cerium group (except europium), worked with a carbon crucible and graphite electrodes. The metals separated by him contained a certain admixture of carbides.

Even the improved electro-chemical methods in use nowadays cannot ensure the production of metals of the high degree of purity required in modern technology. Metallothermic methods are the ones best suited for this purpose.

Fluorides of the rare-earth elements, dehydrated and purified beforehand, are taken as the initial material. Chlorides are

sometimes used, but they are extremely hygroscopic. Moreover, it is difficult to obtain the heavy lanthanides by the reduction of chlorides and the products obtained are not sufficiently pure.\* Reduction with calcium is carried out in special steel "bombs" lined inside with magnesium oxide or in tantalum crucibles with thin walls. Metallic calcium in the form of grains is added in excess of the stoichiometric amount (up to 10 per cent), the batch being carefully mixed. Iodine is added to the reaction mixture because an excess of heat is required for melting the metal obtained and ensuring that it is separated thoroughly and obtained in the form of a compact mass. It is desirable that during the process the reducing temperature exceed the melting point of the metal by at least 250°C. The most suitable temperature interval for reduction, therefore, is 1400–1500°C. Reduction in atmosphere of an inert gas (helium or argon) also has a favourable effect on the yield and purity of metals.

Samarium, europium and ytterbium cannot be reduced to the metallic state by the method mentioned, because crystals of bivalent halides are formed during the process. Moreover, the relatively high volatility of metallic samarium, europium and ytterbium at high temperatures interferes with their reduction. For this reason, in order to produce these metals their oxides are reduced at 1400° in a vacuum with finely divided metallic lanthanum. Lanthanum does not mix with the metal to be reduced because of its low volatility.

Until recent times the production of the overwhelming majority of the pure rare-earth metals did not, as a rule, go beyond the laboratory or industrial experiment scale. As the demand for certain rare-earth elements is increasing every year, it becomes urgently necessary to adapt the methods worked out to the conditions of industrial production where tens and hundreds of kilograms have to be dealt with.

\*This is not strictly true—the purest yttrium metal thus far obtained has been prepared by reduction of the anhydrous chloride by lithium (U.S. Bureau of Mines Report of Investigation 5588, 1960).

## CHAPTER 4

### PRACTICAL APPLICATIONS OF THE RARE-EARTH ELEMENTS

NOT a few cases are known in the history of science where the most important field (or fields) of application of a chemical element was far from being discovered immediately. Let us take germanium, for example. The important part played by it in semi-conductor technology was discovered very recently. Titanium, used chiefly for the preparation of high-quality white mineral pigments ( $\text{TiO}_2$ ) for a long time, has now become the base for heat-resistant non-corrosive alloys. Finally there is uranium, with the really striking evolution of the fields of its application—from colouring glass to its use as the principal nuclear fuel.

For a long time the rare-earth elements did not find extensive application. But nowadays not many of the 88 elements occurring in nature have a range of application as wide as that of the lanthanides. The factors which helped the development of researches on the chemistry of the lanthanides aimed at discovering new fields for their application have already been mentioned in the introduction.

The fields of application of the different elements and their compounds have not yet been completely investigated. The use of radioactive isotopes of the rare-earth elements is still in the initial stages. But interest in this peculiar family of the periodic system has increased remarkably. Suffice it to say that in the last quarter of a century the extraction of concentrates of the rare-earth elements has increased by more than eight times. The rate of production of the lanthanides and their compounds has caught up with that of some non-ferrous and rare metals like molybdenum and tungsten.

While in earlier days the oxides and other compounds of the rare-earth elements were mainly used, the metallic lanthanides are now increasing in importance and usage every year.

Let us begin our story of the various applications of the rare-earth elements in science and industry by going back to the days of Auer von Welsbach about 75 years ago. This chemist was a very practical person. His discovery of a new method of producing incandescent gauzes and mantles for gas lamps laid the foundation of the industrial production of "rare earths" and played an important role in the improvement of lighting. People of the older generation still remember the name "Welsbach mantles". The electric lamp has replaced them but they are still used in some places.

Thus it appears that the first practical application of the rare-earth elements was their use in incandescent mantles and gauzes. The gauzes were prepared from thorium dioxide with an addition of  $\sim 1$  per cent  $\text{CeO}_2$ . This mixture enabled obtaining the maximum illumination.

Another early application of the rare-earth elements may be mentioned. This is the widespread use of ordinary flints for lighters. These are an alloy of iron with 30 per cent cerium—one of the so-called pyrophoric alloys first obtained by the same Auer von Welsbach in 1903. For a long time pyrophoric alloys formed the main sphere of application of the rare-earth elements; they play an important part even today.

Since we have started speaking about alloys of cerium let us begin our survey with the application of the rare-earth elements to metallurgy.

The quality of steel and pig iron depends on their content of O, S, N, P and some other elements. As a rule an effort is made to avoid these elements in the process of melting because they exercise an unfavourable effect on the properties of steel and pig iron, making them more brittle, less ductile and lowering their wear resistance. Various deoxidizing agents and desulphurizers are used to remove these defects. An effort is also made to remove phosphorus and nitrogen. As mentioned already, the rare-earth elements easily combine with non-metals, including those enumerated above. By interacting with O, S, N, P, H, C in the hot state the rare-earth elements vigorously absorb them and thus improve the quality of pig iron and steel.

In these additives the main part is played by cerium, which

is introduced in steels and alloys either in the form of an alloy with iron (ferro-cerium) or in the form of what is known as "misch-metal". The latter is an alloy with a base of rare-earth elements (94–99 per cent) containing also, up to 5 per cent Fe, and traces of Si, C, Ca and Al. Cerium forms up to 65 per cent of the total content of the rare-earth metals.

On the other hand, additions of cerium and other rare-earth metals are used for alloying different brands of steel (heat-resistant, stainless, instrumental) and giving them valuable new properties.

If up to 0·16 per cent cerium is added to pig iron, its yield point is raised considerably and its physico-mechanical properties are improved. This manifests itself particularly in the greater ease with which the iron castings can be treated. Similarly, when 0·75 per cent "misch-metal" is added to steel, its yield point is considerably raised and its workability in the heated state improved. Moreover, this kind of steel acquires additional strength and resistance to oxidation. The effect of additions of rare-earth metals on the various kinds of steel is summarized in Table 10.

In recent times, besides ferro-cerium and "misch-metal", oxides and fluorides of the rare-earth metals have also been widely used as additives.

Alloys of the rare-earth and ferrous metals have similarly found application in industry. The pyrophoric alloys already known to us belong to these. It should be noted that in the main only the alloys of cerium and those with a base of "misch-metal" have pyrophoric properties.\* For example, the composition 49·5 per cent Ce, 44 per cent (La + Nd), 4·5 per cent Fe, 0·5 per cent Al and the remainder—Ca, Si and C possesses pyrophoric properties. Pyrophoric alloys are used in the preparation of igniting devices, tracer bullets and shells, and flints for lighters.

Among other alloys it is necessary to note that steel containing 6 per cent of rare-earth elements is used in the manufacture of surgical instruments, and alloys of iron with cerium and

\*This is not perfectly true. Many other rare-earth alloys, e.g., of the Er-Fe and Y-Fe series, are highly pyrophoric.



manganese are characterized by their small coefficient of expansion.

We have given the reader an account of the application of rare-earth elements to ferrous metallurgy. They are no less important in non-ferrous metallurgy where they find diverse applications.

TABLE 10

*Effect of additives of rare-earth metals on the properties of different steels*

Type	Additive	Nature of change	Remarks
Stainless austenite steels	Misch-metal (ferro-cerium)	Greater fluidity no red-shortness, higher plasticity, rolling and forging easier.	
High-speed	Misch-metal	Rolling and forging much easier.	
Stainless austenite steels with high Cr and Ni content	Misch-metal	Improved plasticity in heated state, higher heat-resistance and corrosion resistance.	No more than 0.2% misch-metal is needed for a content of 5-40%

Because of their high reducing capacity, they can be used in metallothermic reactions. Cerium is a more active reducing agent than aluminium. It is true that lanthanido-thermic processes have not yet found application in industry, but laboratory experiments have shown that it is possible by this means to obtain sufficiently pure Nb, Zr, Fe, Co, Ni, Cr, Mn, Y, W and U and also B and Si. As de-oxidizing agents the rare-earth metals are better than silicon and aluminium and are widely used for de-oxidation of copper and its alloys.

Alloys of the rare-earth elements with aluminium and magnesium have found wide application, Here too the most important role belongs to cerium. It is interesting to note that the alloy Al-Ce was first obtained in 1904. The use of the alloy

Al-Ce for pistons of aircraft engines was the first important technical application of the rare-earth elements in non-ferrous metallurgy. Addition of cerium and "misch-metal" to aluminium alloys raises their yield point and helps to improve their physico-mechanical characteristics; the fatigue resistance is increased and the formation of cracks is prevented. It has also been established that the addition of only  $\frac{1}{2}$  per cent of rare-earth metals to alloys of aluminium containing up to 9 per cent of magnesium considerably increases their corrosion resistance. Generally speaking, such aluminium alloys are widely used in machine parts where high tensile strength at this temperature is required.

No less interesting are the alloys of magnesium and the rare-earth metals.

It is not without reason that magnesium is called the metal of the future. It can already be considered the metal of our age to a considerable extent. Magnesium alloys are very light as construction materials and possess at the same time a high strength factor exceeding that of aluminium alloys and many steels. The principal magnesium alloys used in industry are formed with the system Mg-Al-Zn as the base.

One defect of the magnesium alloys used is the somewhat limited range of temperature over which they can be used, the upper limit being  $150^{\circ}$ . It is therefore very important to produce magnesium alloys capable of working at  $250-350^{\circ}$ . The use of the rare-earth elements proved very helpful in this respect.

Metals of the cerium group have found application in the production of very light heat-resistant magnesium alloys. The effect of additions of rare-earth metals (La-Nd) on the mechanical properties of magnesium alloys (Mg + 8.5 per cent Al, 0.5 per cent, Zn and 0.2 per cent Mn) at  $250^{\circ}$  is shown in Fig. 14.

As can be seen from the figure, the heat resistance of such alloys increases slightly on adding lanthanum; additions of cerium and praseodymium lead to a sharp increase in the heat resistance, and this increases still further on passing over to neodymium. It should be noted that increase in the strength of the magnesium alloys also is particularly marked when neodymium is used. This effect of neodymium is explained by its high

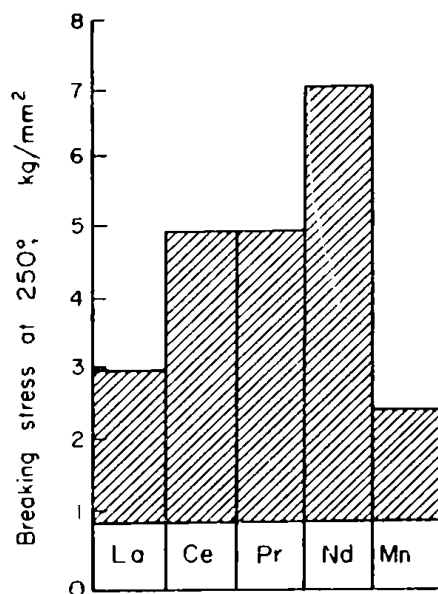


FIG. 14. Effect of additions of rare-earth metals on the mechanical properties of magnesium alloys: alloy ML5 (Mg + 8.5% Al, 0.5% Zn, 0.2% Mn); additions of rare-earth metals  $\sim 3\%$ .

solubility in magnesium, which ensures the best mechanical properties for the alloy. Additions of the rare-earth elements thus raise the heat-resistance of the magnesium alloys by raising the upper temperature limit by  $100^\circ$ . In practice “misch-metal” (50–65 per cent Ce), which is cheaper, is generally used. It exercises an almost similar effect.

Magnesium alloys with an addition of rare-earth elements are used in jet technology and in the aviation industry, in machine parts where good casting qualities are required together with high heat resistance.

Alloys of the rare-earth elements with many other non-ferrous and rare metals are still in the stage of laboratory investigation. But reports on the favourable effect of the addition of rare-earth elements to such metals have appeared in literature. Thus it was found that 0.2 per cent Ce improves the mechanical properties of copper; the introduction of 0.2–2 per cent of rare-earth metals in nickel alloys increases their resistance to oxidation at high temperatures. Additions of cerium to cobalt alloys increase the heat resistance of these alloys so much that

they can be used for making turbine blades in jet engines. Finally, alloys of the rare-earth metals with copper and silver can be used for making thermo-couples.

The effect of the different rare-earth elements on the magnetic properties of the magnesium alloys has been noted. Thus, for example, the alloy of magnesium with gadolinium is distinguished by its magnetic characteristics.\*

In the last few years intensive researches have been started on systems formed by the rare-earth elements and the actinides. On the basis of these researches it has been shown that it is possible in principle to extract plutonium from liquid uranium with the help of fused lanthanum, cerium and neodymium. This method cannot compete at present with the extraction of plutonium with the help of liquid silver or a fused mixture of fluorides of U, Ca and Li. It has great prospects however, since it promises to make plutonium considerably cheaper.

The rare-earth elements have found extensive application in the chemical industry. One of these—utilization of their catalytic activity—has been known for a relatively long time, but it is only in the last decade that it has become of practical value. The compounds of cerium have been studied more closely than the other compounds. As a rule, rare-earth elements are used as additives (promoters) to other catalysts and considerably increase the catalytic activity of the latter. But the oxides (and in certain cases the salts) of some rare-earth elements are often used as independent catalysts. Thus cerium dioxide is one of the best catalysts for promoting the hydrogenation of CO at high pressures, it also catalyses the dehydrogenation reaction of alcohols.

Praseodymium oxide,  $\text{Pr}_2\text{O}_3$ , has a catalytic effect on the low-temperature oxidation of ammonia. The oxides of La, Pr, Nd, Gd and Dy as well as those of other elements of the yttrium group have also been found to exercise a significant effect on the dissociation of ethyl alcohol. An interesting example of the catalytic effect of cerium is the considerable acceleration of electro-

\*These statements are difficult to rationalize, there being few metals whose magnetic properties are not "characterized" by the addition of gadolinium, the most "magnetic" of the rare earth metals and which possesses a higher saturation magnetization than iron.

chemical oxidation of aniline in quinone in the presence of cerium ions. Cerium sulphate, together with a mixture of sulphates of elements of the cerium group, is a fairly good catalyst for the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$ .

Salts of the rare-earth elements were proposed as catalysts in the synthesis of ammonia and for some oxidizing processes in organic chemistry. Lanthanum manganate  $\text{La}(\text{MnO}_4)_3$  was used for the catalytic oxidation of CO on the basis of theoretical considerations. Very interesting catalytic properties have been predicted for the compounds of dysprosium and holmium.

The range of application of the rare-earth metals and their compounds as promoters is very wide. Promoters are additions which intensify the activity of some well-known catalysts. For example, a cobalt catalyst with the addition of  $\text{La}_2\text{O}_3$  (up to 10 per cent) is more effective for the synthesis of liquid hydrocarbons from CO and  $\text{H}_2$  than a similar catalyst used earlier,  $\text{ThO}_2$  with a promoter.

Additions of  $\text{La}_2\text{O}_3$  (less than 10 per cent) to the catalyst  $\text{MgO} + \text{SiO}_2$  increase the yield of octane during the cracking of gas oil, as the following comparison shows:

Catalyst	Yield of octane, %
$\text{SiO}_2, \text{MgO}$	43.1
$\text{SiO}_2, \text{MgO} + \text{La}_2\text{O}_3$	78.1

i.e., the yield is almost doubled.

The dehydrogenation of hydrocarbons on  $\text{Al}_2\text{O}_3$  with neodymium as promoter is considerably accelerated.

Investigations on the catalytic and promoting action of the rare-earth elements are still in a relatively early stage. It cannot be doubted, however, that fresh advances will be made in the coming years which will increase still further the importance of these elements, long considered useless for practical purposes.

Another important application of the rare-earth elements, also pertaining to the chemical industry, is the synthesis of crystallo-phosphors. We may remind the reader that this is the common name for substances whose function consists in the conversion of different forms of energy into light energy. Because of this they are used in coatings of luminescent lamps, for the painting of screens of cathode-ray tubes (oscillographs,

television and radar valves, etc.) and for the study of radioactive radiations. As luminescence is the name given to the phenomenon of cold glow of a substance under the action of various forms of energy, the most luminous substances are called luminophores. They are obtained by calcining a solid mixture of a base, a flux and an activator.

Investigations have shown that the rare-earth elements can be used as excellent activators of luminophores, and in some cases their salts can be used as bases. All the rare-earth elements can function as activators, the most valuable being cerium and europium in the form of compounds. The salts of La, Ce, Eu and Sm give compositions exhibiting luminescence in the red and infrared regions.

Obviously we cannot speak of the advantages of the rare-earth elements over other activators used earlier. But the use of the rare-earth elements for this purpose has considerably extended the range of possible activators and in a number of cases it has been found possible to produce luminophores with fairly specific properties, e.g., deflagrating luminophores of the composition  $\text{SrS}$  (base)—Sm, Eu (activators) which can react to excitation at  $0.005$  röntgen produced by  $\gamma$ -rays.

The use of the rare-earth elements for the manufacture of lakes and dyes, and particularly paints for porcelain, may be considered as comparatively "ancient" applications of the rare-earth elements. The oxides and the compounds of the rare-earth elements give them the following shades:

Compounds of the rare-earth elements	Colour
Cerium group (oxides)	Light-brown
Salts of praseodymium	Green
Salts of neodymium	Reddish
Neodymium phosphate	Flesh
Cerium titanate	Yellow
Cerium molybdate	Light yellow
Cerium tungstate	Greenish blue

Additions of some salts of the rare-earth elements (cerium naphthenate) in small quantities help a number of varnishes to dry quickly and retain their transparency for a long time.

The rare-earth elements play an important part in the manufacture of glass, for both ordinary and special purposes, and in the production of ceramic ware and abrasives. Mixed, as well as single oxides, are used for the production of different kinds of glass. Here too  $\text{CeO}_2$  is of fundamental importance. We get further proof that cerium is the rare-earth element with the widest practical application.

Cerium dioxide has been used for decolourizing glass for many years. Many colourless industrial glasses have a low light transmission factor due to the presence of some compounds, particularly those of iron. In such a case, not only the concentration of iron but also its valency affects the colour and transparency of the glass. Thus compounds of  $\text{Fe}^{2+}$  absorb light ten times more strongly than compounds of  $\text{Fe}^{3+}$ . The absorption can be removed (by converting  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ ) by creating in the mass of glass an oxidizing atmosphere by introducing in the batch arsenic and antimony oxides in small doses. But removal of one unpleasant factor may bring in another: the appearance of bubbles and "pockets" in the glass mass due to the excess of oxygen from  $\text{Sb}_2\text{O}_5$  and  $\text{As}_2\text{O}_5$ . Moreover, glasses containing arsenic quickly become yellow under the action of the sun's rays and become quite turbid under the action of  $\gamma$ - and X-rays.

The decolourizing action of  $\text{CeO}_2$  is explained by its strong oxidizing capacity, which ensures the conversions of a considerable part of the iron into the colourless form  $\text{Fe}^{3+}$ .

Since pure  $\text{CeO}_2$  is costly, cerium preparations containing impurities of  $\text{La}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$  and  $\text{Pr}_2\text{O}_3$  and oxides of some other rare-earth elements, having almost the same effect but cheaper and more easily available, are used in the manufacture of commercial glass.

Glasses containing  $\text{CeO}_2$  possess the property of not losing their transparency on prolonged exposure to the sun and also to the action of radiation of a wide range of energy.\* This is explained by the fact that the absorption caused by exposure does not occur in the visible region of the spectrum. Figure 15 shows the effect of the addition of  $\sim 1$  per cent  $\text{CeO}_2$  on the stability of the glass to  $\beta$ -radiation. For this reason, cerium

\*Unless arsenic or antimony also are present.

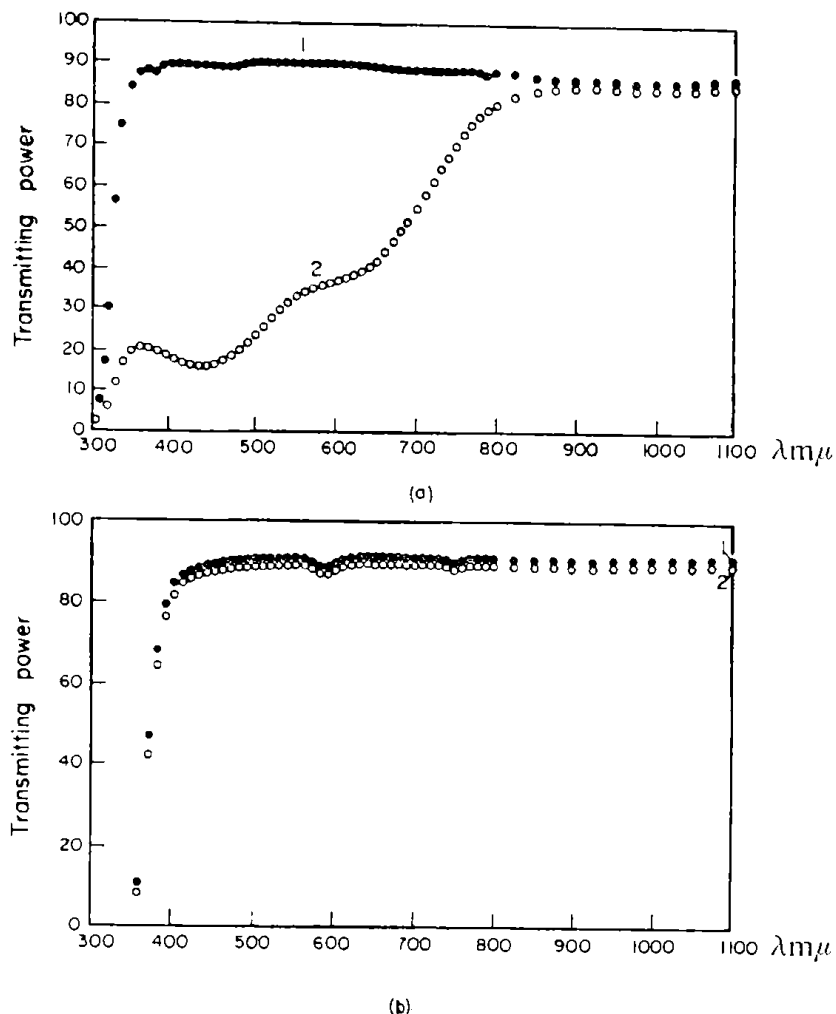


FIG. 15. Effect of adding  $\sim 1\%$   $\text{CeO}_2$  on the resistance of glass to  $\gamma$ -radiation.

a—transmitting power of glass without addition of  $\text{CeO}_2$  (1) before and (2) after irradiation; b—1%  $\text{CeO}_2$  added.

dioxide is used in the preparation of protective transparent glass blocks in nuclear technology.

Because of the capacity of glasses with additives of the rare-earth elements to absorb ultraviolet rays they are used for special purposes, e.g. for making sun-glasses (Nd), in glass-blowing and welding work (Nd + Pr), for glasses protecting the eyes from neutron radiation (Gd, Sm) etc.

Boro-silicate glasses, containing  $\text{La}_2\text{O}_3$ , have a high refractive index. Glasses with additions of  $\text{Nd}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  are used for the preparation of special optical systems. The attempts to produce glasses with the system of oxides  $\text{Li}_2\text{O}-\text{La}_2\text{O}_3-\text{SiO}_2$ , not



containing the alkaline earth metals, as the base are extremely interesting. Such glasses have high strength and good electrical conductivity. Finally, oxides of the rare-earth elements are used for the production of artificial gems.

When we spoke of the decolourizing action of  $\text{CeO}_2$  we had in mind an amount not exceeding 0·8–1 per cent of it in the glass. Above this concentration cerium oxide begins to exercise the opposite effect by imparting a brown colour to the glass. Large concentrations of Nd oxide have a similar effect, giving a deep red shade to the colour,  $\text{Pr}_2\text{O}_3$  gives a green, and a mixture of  $\text{Nd}_2\text{O}_3 + \text{Pr}_2\text{O}_3$  a blue shade.

In recent times the rare-earth elements have begun to be widely used in the ceramic industry. Cerium sulphide, with a very high melting point ( $\sim 2000^\circ$ ), is used for the preparation of special crucibles for melting metals in a reducing atmosphere at temperatures up to  $1800^\circ$ .

The oxides of the rare-earth elements reduce the cracking of glazes and impart different colours to them.

A very large field of application of the rare-earth elements in the silicate industry is their use as abrasives for polishing glass. An abrasive, consisting of oxides of the rare-earth elements, is called "Polirite" and has the following composition:

Oxides	Content, %
$\text{CeO}_2$	40–47
$\text{La}_2\text{O}_3, \text{Nd}_2\text{O}_3, \text{Pr}_2\text{O}_3$	58–41
Others ( $\text{SiO}_2, \text{Al}_2\text{O}_3, \text{CaO}, \text{Fe}_2\text{O}_3, \text{MgO}$ )	$\sim 2$

Other materials were used earlier for polishing glass—oxides of various metals ( $\text{CuO}, \text{Al}_2\text{O}_3, \text{ZnO}, \text{Cr}_2\text{O}_3, \text{Ni}_2\text{O}_3, \text{Mn}_2\text{O}_3, \text{ThO}_2$ ), so-called iron crocuses, etc. Comparison of their polishing capacity with that of "Polirite" shows that this has the highest polishing capacity, about 1·5–2 times greater than that of the others. A number of types of "Polirite" for treatment of the surface of different kinds of glass are known. The speed of polishing is considerably increased when "Polirite" is used.

We are witnessing the incursion of the rare-earth elements into such leading branches of industry as electrical and radio engineering and electronics. Fluorides of the rare-earth elements (mainly cerium again!) are used in the electrical industry for the

manufacture of electrodes of arc lamps and projectors. Additions of rare-earth elements considerably increase the life of Nichrome wires, which are widely used in daily life (heating devices). In the electrical lamps industry the rare-earth elements are used as absorbers of gases (called getters). Borides of the rare-earth elements ( $\text{LaB}_6$  and  $\text{GdB}_6$ ) are used as material for the cathodes of electronic devices with a long period of activity. Cerium oxide mixed with  $\text{TiO}_2$  is a good dielectric, while mixed with  $\text{SrO}$  it can be used for the manufacture of radio-ceramic materials. Finally, the magnetic properties of dysprosium and its compounds and the super-conductivity of lanthanum are some of the applications, as yet few, of the rare-earth elements in radio engineering and electronics.

Workers in the textile and leather industries are familiar with certain compounds of the rare-earth elements. For example, the salts of  $\text{Ce}^{4+}$  are used for dyeing leather; cerium nitrate is used as a mordant for alizarin dyes. Chlorides and acetates of the rare-earth elements make textile fabrics and artificial cloth waterproof and make them resistant to the action of acid solutions and vapours. A number of salts are used as tanning agents.

In agriculture the salts of the rare-earth elements are used as insecto-fungicides and micro-fertilizers.

Finally, medicine also is a field where the compounds of rare-earth elements have long penetrated. Many medicines produced for the treatment of tuberculosis, cancer, leprosy, eczema and rheumatism contain lanthanides. Some rare-earth salts have been found to exercise an antiseptic action. The best known are the salicylates of neodymium and praseodymium (called "Dimal") which are useful germicides. Cerium salts are used for the treatment of vomiting and sea-sickness. Some salts of the rare-earth elements prevent blood from clotting, which makes them valuable for the conservation of blood. The salts of erbium and cerium increase the haemoglobin content and the number of red corpuscles in the blood. The salts of some rare-earth elements are used for embalming.

Among the other applications of the rare-earth elements must be mentioned the extensive use of quadrivalent cerium in analytical chemistry. Compounds of  $\text{Ce}^{4+}$  are used for oxidation-

reduction titrations (one of the forms of oxidimetry is cerimetry). Salts of  $\text{Ce}^{4+}$  are used in photography.

Perhaps one of the most surprising uses of the rare-earth elements, at present of purely scientific interest only, is their application for the production of very low temperatures. Gadolinium sulphate or chloride, strongly paramagnetic substances, are placed in a well-insulated space filled with an inert gas (generally helium) and a magnetic field is switched on. The salt is heated as a result, the gas absorbs the heat and is pumped out and the magnetic field is switched off. The gadolinium salt is thus cooled to a temperature lower than the initial temperature. This cycle is repeated several times. The data available shows that a temperature very close to absolute zero ( $0.0002^\circ\text{K}$ ) can be attained.

And with that we could have finished our survey, far from short now, of the various applications of the rare-earth elements if . . . If the tremendous advances in nuclear physics had not been made: the synthesis of new elements, the solution of the problem of harnessing nuclear energy, the production of a large number of radioisotopes. All these factors have greatly extended the scope of application of the rare-earth elements. New and completely unexpected properties were discovered and these raised the problem of utilizing these properties for the welfare of mankind.

One of the uses of the rare-earth elements which owe their origin to the development of nuclear technology is the extraction of plutonium from liquid uranium. We have already mentioned this. In what follows we shall consider new methods of the application of these elements in 3 aspects: the use of the rare-earth elements for the separation of the transuranic elements; the application of radioactive isotopes of lanthanum and the lanthanides, and finally rare-earth metals as materials for nuclear reactors.

A large number of radioactive isotopes of practically all the elements of the periodic system were obtained in the last 20 years. But it is one thing to produce a certain isotope with the help of nuclear reactions, and another to isolate this isotope, so to speak, in the pure state. The problem is complicated by the fact that radioisotopes are obtained in micro-chemical quanti-

ties and the usual methods of classical chemistry, which have to deal with macro-quantities, are inapplicable. Here radiochemical methods come to the help of the research worker. One of the most developed among these is the method of co-precipitation, based on adding so-called carriers to a solution containing a radio-isotope. When a suitable reagent reacts with the solution the carrier precipitates, carrying with it the ions of the given isotope. Carriers may be isotopes or otherwise. The first class implies stable isotopes of the given element (e.g. the stable isotope  $\text{I}^{127}$  is used for the separation of the radioactive  $\text{I}^{128}$ ). Non-isotopic carriers are used in cases where radioactive isotopes do not have corresponding stable counterparts (as, for example, the majority of the transuranic elements, astatine, etc.). In such a case other elements, with similar properties, are used. The rare-earth elements as we shall see later, resemble the actinides in many respects and can therefore be used as non-isotopic carriers for the separation of radioactive isotopes of the actinides.

Let us illustrate what has been said with the help of an example.

When uranium is irradiated with neutrons, the nearest transuranic elements, neptunium and plutonium, are formed in appreciable quantities. The difference in the valency states of these elements is used for separating them from the irradiated uranium;  $\text{Np}^{4+}$  or  $\text{Pu}^{4+}$  precipitate together with  $\text{LaF}_3$ , while  $\text{U}^{6+}$  remains in the solution. Thus in the given case lanthanum acts as a non-isotopic carrier. We might mention that another method of co-precipitation of tri- and quadrivalent Np, Pu and Am with the help of  $\text{K La}(\text{SO}_4)_2$  is in use.

The application of the radioisotopes of the rare-earth elements is of great interest and full of prospects. This is a very new field but here also a number of important achievements may be noted. Chief among these are the utilization of  $\gamma$ -radiation from  $\text{Tm}^{170}$ ,  $\text{Eu}^{155}$  and  $\text{Ce}^{144}$  for medical diagnosis and defectoscopy.

Everybody knows how complicated and numerous the equipment of an X-ray chamber is. The X-ray apparatus used in medicine requires a source of electric current, is not portable and therefore needs stationary conditions. Meanwhile the

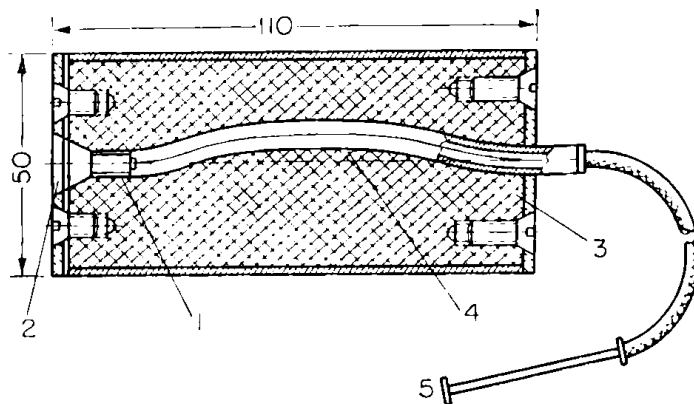


FIG. 16. Portable radioscopy apparatus with the gamma-emitting radioisotope  $\text{Tm}^{170}$ .

1—preparation  $\text{Tm}^{170}$ ; 2—Plexiglas window; 3—lead casting; 4—steel tube; 5—discharge pipe.

demand for light, compact X-ray apparatuses is very great. This is where the isotope  $\text{Tm}^{170}$ , comes to one's aid. It has a soft  $\gamma$ -radiation closely resembling X-ray radiation. A radioscopy apparatus using  $\text{Tm}^{170}$  is shown in Fig. 16. As can be seen the construction of the apparatus is extremely simple. A steel tube with a preparation of  $\text{Tm}^{170}$  (weighing 0.1–0.2 g) is placed in a protective lead casing connected with a discharge pipe. A slight pressure on the discharge tube displaces the preparation of  $\text{Tm}^{170}$  towards the plexiglass window and makes radiation possible. The advantages of such an apparatus are its lightness (it weighs about 3 kg, mainly because of the lead casing), portability, independence of a source of current and finally, extreme simplicity of operation, not requiring any special training on the part of the operator.

Moreover, the used "charges" of  $\text{Tm}^{170}$  (its half-life is 129 days) can be regenerated by repeated irradiation with neutrons.

Unfortunately radioscopic equipment using thulium cannot be used over such a wide range as the ordinary X-ray equipment. Besides, photographs taken with these apparatuses require a long exposure time. But for relatively simple cases of radioscopy (bone tissues) the use of  $\text{Tm}^{170}$  is highly effective. 100,000 thulium "X-ray tubes" are being produced in the U.S.A. nowadays.

Soviet scientists have proposed a method of intensification of  $\gamma$ -radiation from  $\text{Tm}$  based on the use of a special integrating

photo-electric apparatus. Such a combination ensures obtaining photographs with sharp contrasts and can be used for the early detection of new pathological formations in an organism (cancerous tumours, etc.).

It has also been shown that the radioactive isotope  $\text{Eu}^{155}$  (with a half-life of 1.7 years) can be used for X-ray diagnosis.

$\text{Tm}^{170}$ ,  $\text{Eu}^{155}$  and  $\text{Ce}^{144}$  are being widely used in  $\gamma$ -defectoscopy, in testing the quality of thin-walled machine parts made of aluminium and steel. It may be noted that the sensitivity of  $\text{Tm}^{170}$  in a thickness of the specimen not greater than 6 mm is much greater than that of any other known radioisotope. When  $\gamma$ -rays of  $\text{Tm}^{170}$  and  $\text{Eu}^{155}$  are used for the radioscopy of steel with a thickness up to 15–20 mm, titanium alloys up to 30–40 mm, aluminium alloys up to 50–60 mm the sensitivity

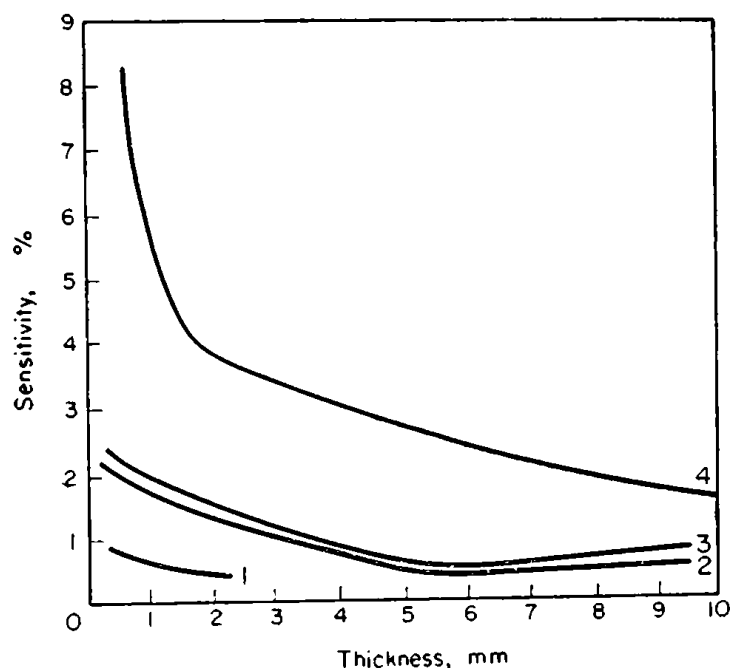


FIG. 17. Sensitivity of steel on irradiation with  $\gamma$ -rays of some radioisotopes.

1— $\text{Ce}^{144}$ ; 2— $\text{Tm}^{170}$ ; 3— $\text{Eu}^{155}$ ; 4— $\text{Ir}^{192}$ .

of the method is 2–4 times greater than when well-known radioisotopes like  $\text{Ir}^{192}$ ,  $\text{Cs}^{137}$  and  $\text{Co}^{60}$  are used. This is illustrated by Fig. 17.

$\gamma$ -rays from  $\text{Tm}^{170}$  have been widely used in archaeology. Characters and symbolic signs have been found in the bronze-

lining of an Assyrian helmet of the 9th century B.C. These could not have been discovered by any other method.

The reader is already familiar with the history of the element 61, promethium, the last of the rare-earth elements, which has not yet been found on the earth's surface. Paradoxical though it may appear, there are grounds for supposing that the radio-isotope of promethium  $\text{Pm}^{147}$  will become one of the most promising isotopes of the rare-earth elements. At the moment it has begun to be used in the production of atomic batteries.

The atomic battery is based on the transformation of the energy of radioactive disintegration into electrical energy. In theory there can be a number of methods for such a transformation. In one of the designs, for example, the electric current arises as a result of the appearance of a potential difference between the positively charged sources of radiation (because of the escape of  $\beta$ -particles) and the negatively charged collector of the electrons (the source of activity is  $\text{Sr}^{90}$ ).

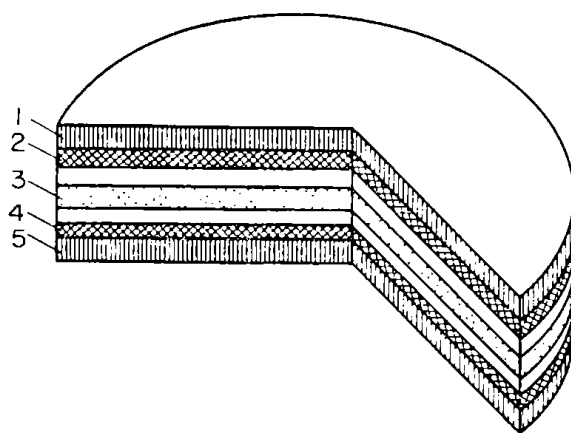


FIG. 18. Atomic battery working on  $\text{Pm}^{147}$ .

1—negative layer of upper silicon photo-element (s.p.);  
2—positive layer of upper s.p.; 3—radioactive layer; 4—  
positive layer of lower s.p.; 5—negative layer of lower s.p.

Figure 18 shows an atomic battery working on promethium. It has miniature dimensions. The disk is as large as the top of an ordinary drawing pin and the thickness is hardly greater than 1 mm. The principle of operation of the battery consists in the transformation of the energy of  $\beta$ -disintegration of  $\text{Pm}^{147}$  into light energy and later into electrical energy. The source of

light consists of a finely powered mixture of phosphorus and  $\text{Pm}_2^{147}\text{O}_3$  (promethium oxide is taken in a quantity  $\sim 5$  mg); the  $\beta$ -particles are absorbed by phosphorus and converted into red or infrared light. Sometimes a special luminophore (e.g. cadmium sulphide) is used instead of phosphorus. The luminescence is captured by two or more silicon photo-elements and converted into electric current. The initial capacity of a promethium battery amounts to  $20 \mu\text{W}$  at a voltage of  $\sim 1\text{V}$ .

Changes in temperature, pressure and other external conditions do not affect the working of the battery. It is interesting to note that at a low temperature ( $-93.3^\circ$ ) it works even better than at room temperature. Such a battery can produce electrical energy for at least 5 years.

The ways in which atomic batteries can be used are extremely varied: in portable semi-conductor circuits, miniature receivers, apparatus for working at high altitudes, oceanographic investigations, guided missiles. Batteries with  $\text{Pm}^{147}$  are used in the construction of hearing aids. Comparison of promethium batteries with batteries working with other radioisotopes leads us to prefer the first, mainly because of its small dimensions.

The high cost of promethium is a drawback of the  $\text{Pm}^{147}$  battery. Many radioisotopes of the rare-earth elements are used as radioactive indicators, e.g. for the study of co-precipitation processes, chromatographic separation of lanthanides—among which mention should be made of  $\text{La}^{140}$ ,  $\text{Ce}^{141}$ ,  $\text{Eu}^{152}$ ,  $\text{Tb}^{160}$ . The use of  $\text{Ho}^{166}$  and  $\text{Dy}^{165}$  (as radioactive indicators) in analytical chemistry has been noted.

The development of nuclear technology made it imperative for scientists and engineers to look for new construction materials, particularly for the controlling rods of nuclear reactors. It was found that an alloy of stainless steel with gadolinium is most effective for this purpose. When the capture cross-sections for thermal neutrons ( $\sigma$ ) of the different elements (see p. 106) are considered, it is easily noted that gadolinium has the largest cross-section (of the order of 44,000 barns). This is considerably larger than the value of  $\sigma$  for B (3000 barns) and Cd (2500 barns) which are also used in regulating rods. The possible use of the heavy rare-earth elements, in which the cross-section does not



decrease with increase in the energy of the neutrons as rapidly as in other elements, is of some interest.

The history of the application of the rare-earth elements has run along an interesting course from Welsbach mantles to atomic batteries. Only 60 years have passed since specimens of some rare-earth metals were exhibited at the International Exhibition in Paris as testimony of the achievements of chemistry in separating these, as it seemed, extremely rare elements with a limited range of application in practice. And now we are witnessing the vigorous penetration of the rare-earth elements into different branches of science and industry.

## CHAPTER 5

### THE PRESENT STATE OF THE PROBLEM OF THE RARE-EARTH ELEMENTS

#### 1. Once More on the Position of the Rare-earth elements in the Periodic System

Let us return once again to the main snag in the periodic system, the problem of placing the rare-earth elements in Mendeleev's table.

The brilliant work of Moseley and Bohr and the subsequent theoretical investigations determined finally the number of rare-earth elements and gave a physical interpretation of the existence of this peculiar family of the periodic system.

The rare-earth elements had come to be considered as a kind of inter-periodic group (in Bohuslav Brauner's words). They were placed in the box containing lanthanum under the number 57 in Mendeleev's table.

It would seem everything was simple and clear, that such a position does not interfere with the internal logic of the periodic system. All the same it is impossible to consider this arrangement as a final solution of the problem, because certain important points remain somewhat obscure. For example, there is no indication of the existence of anomalous valencies in the rare-earth elements which is particularly important in the case of cerium. The presence of a certain periodicity inside the family is also not emphasized. It is therefore understandable that there should be attempts to shed more light on the position of the rare-earth elements in Mendeleev's table.

Among these attempts the proposals of Spencer, Klemm and Pearce deserve the greatest attention. Spencer's arrangement of the rare-earth elements (1928) is shown in Fig. 19.

Spencer's merit lay in the fact that in trying to solve the problem of the arrangement of the rare-earth elements he did not proceed to change the construction of the periodic system.

Series	GROUPS											
	II			III			IV			V		
	A		B	A		B	A		B	A		B
4	Ca			Sc			Ti			V		
5			Zn			Ga			Ge			As
6	Sr			Y			Zr			Nb		
7			Cd			In			Sn			Sb
8	Ba			La			Ce, Pr Nd, 61			—		
9		—		Sm, Eu, Gd				Tb		—		
10				Dy, Ho, Er Tm, Yb, Lu			Hf			Ta		

FIG. 19. Arrangement of rare-earth elements in Mendeleyev's table (Spencer, 1928).

He did not try to build a space model like most other scientists before him and attempted to solve the problem within the framework of the generally accepted existing table with the help of some chemical and physical characteristics.

Spencer proceeded from a consideration of three factors: (1) the solubility of the sulphates of the rare-earth elements in alkaline sulphate solutions; (2) the curves of the magnetic moments of the rare-earth elements (see Fig. 10) and (3) anomalies in their valencies. Elements, the magnetic moments of which are situated on the first curve (most of the elements of the cerium group), are situated in the 8th row of the table. Elements on the rising branch of the 2nd curve (terbium group elements) are situated in the 9th row, and the remaining (yttrium group elements) in the 10th row.

Thus lanthanum occupies a position in the 8th row, subgroup IIIA, because its oxide is the most basic of all the oxides of the rare-earth elements. Ce, Pr and Nd in Spencer's opinion

should be placed in sub-group IVA of the same row, because, like Ti and Zr, they form two oxides— $\text{Me}_2\text{O}_3$  and  $\text{MeO}_2$ ; Element 61 also should be placed here because its magnetic moment lies between Nd and Sm. Further, Sm, Eu and Gd are situated in the 9th row because of the existence of the bivalent state in samarium and europium as in Ga, In and Tl. The chemical behaviour of gadolinium is similar to that of (trivalent) samarium. Spencer pointed out that gadolinium was separated by de la Fontaine from Mosander's didymium together with samarium. The remaining six elements—Dy, Ho, Er, Tm, Yb, Lu—are placed in the 10th row, in sub-group IIIA.

But in point of fact Spencer's proposal was not a very successful attempt to "break out" from the limits of a box of the periodic system. Klemm's idea (1932) was a considerable step forward. On the basis of magneto-chemical considerations he proposed to divide the family of rare-earth elements into two groups Ce to Gd and from Tb to Lu respectively. According to Klemm, the trivalent ions of lanthanum, gadolinium and lutetium form electron configurations which play a special role in this scheme, like the inert gases in Mendeleyev's system.

On the basis of his scheme Klemm showed that the properties changed smoothly from one to the other in accordance with the magnetic data. He also succeeded in explaining the existence of the anomalous valencies of certain lanthanides and predicting the bivalent state of ytterbium which was soon confirmed. Klemm's scheme formed the basis of the "periodic system" of the ions of the rare-earth elements of which we have spoken earlier (pp. 38, 39.)

In 1935 Pearce put forward the idea of arranging all the 15 rare-earth elements in the box for lanthanum in accordance with the anomalous valencies appearing in them. The distribution of the rare-earth elements according to Pearce is shown in Fig. 20.

The "central" position in the box of element 57 is occupied by La, Gd and Lu, which correspond to sub-group IIIA most closely because of their stable electron configuration. On the left of the three "central" elements are situated elements with a tendency to exhibit an anomalous valency of  $2+$ , on the right those with  $4+$ . Thus the elements "on the left" are associated

Zn		Ga	
	Y		Zr
Cd		In	Sn
	La Ce Pr Nd 61 Sm Eu Gd Tb Dy Ho Er Tm Yb Lu		Hf
Hg		Tl	Pb
	Ac		Th

FIG. 20. Arrangement of rare-earth elements in the periodic table (Pearce, 1935).

with those on the second, as it were, and those “on the right” with the fourth group of the periodic system.

Although the allocation of the rare-earth elements in one box of the periodic system is generally recognized, to a certain extent it does destroy the orderliness of the table and the exclusive character of this family is not sufficiently reflected. Evidently any attempt at a final solution of the problem should consist, firstly, in a careful study of the properties of the different rare-earth elements and, in particular, the conditions under which anomalous valencies appear, and secondly, in a thorough comparison of the properties of the lanthanides with those of the actinides—a family which in many ways reminds one of the rare-earth elements.

## 2. Lanthanides and Actinides

As early as in 1923 Niels Bohr predicted the possibility of the existence of a family of elements similar to the rare-earth elements, i.e., formed by the filling of the  $5f$ -subshell, situated deep below, in the seventh period. It would be logical to suppose

that the first member of the new family would be thorium ( $Z = 90$ ), since actinium ( $Z = 89$ ) is the analogue of lanthanum.

But at that time the chemical and physical properties of the elements at the end of the periodic system had not been studied properly and data on the electronic structure were practically absent. It was therefore impossible to determine precisely from which element of the seventh period the formation of the  $5f$ -subshell would begin.

The first attempt to shed light on this question was made by Segré and Urey. In 1926 they arrived at the conclusion that the filling of the  $5f$ -subshell should not begin before the element with  $Z = 95$ , an element not known at that time. Seven years later Wu and Goudsmit shifted the beginning of the new family by two elements to the right and in 1937 V. Goldschmidt indicated the possibility of the appearance of the first  $5f$ -electron in proto-actinium or thorium. Finally in 1941, the distinguished theoretical physicist Maria Heppert-Meyer announced that "theory predicts the appearance of the second 'rare-earth group' in the neighbourhood of  $Z = 92$ . The first occupied  $5f$ -level should appear in  $Z = 91$  or  $92$ ." This announcement was in agreement with the inference of Eibelson and Macmillan who artificially produced the first transuranic element neptunium. On the basis of the chemical similarity between uranium and neptunium they reasoned that the new family should begin with uranium.

The subsequent artificial production of other transuranic elements raised the practical question of where to locate the new family in the periodic system. Two main approaches to the problem were made. One of them—the actinide hypothesis—considers actinium as the first member of the new family and implies the appearance of the first  $5f$ -electron in thorium; the second, the uranide hypothesis, calls uranium the first member of the new family. Both of these hypotheses found authorities to support them.

We shall not go into the numerous pieces of evidence adduced by the supporters of these hypotheses. A great deal of literature exists on the subject and to this we refer the reader. But two points should be noted. First of all, spectroscopic data do not as yet give an unambiguous answer to the question in which of

these elements the 5*f*-electron will appear. The final answer will possibly be found when the 103rd element is produced artificially and its properties studied, because the second "rare-earth" family should apparently end with this element. The main thing that should interest us is that study of the properties of the actinide elements has shown that they are remarkably similar to the rare-earth elements. This, in its turn, has made it necessary to study the different lanthanides more carefully. A proper knowledge of the properties of the second rare-earth family is impossible without a thorough knowledge of the first.

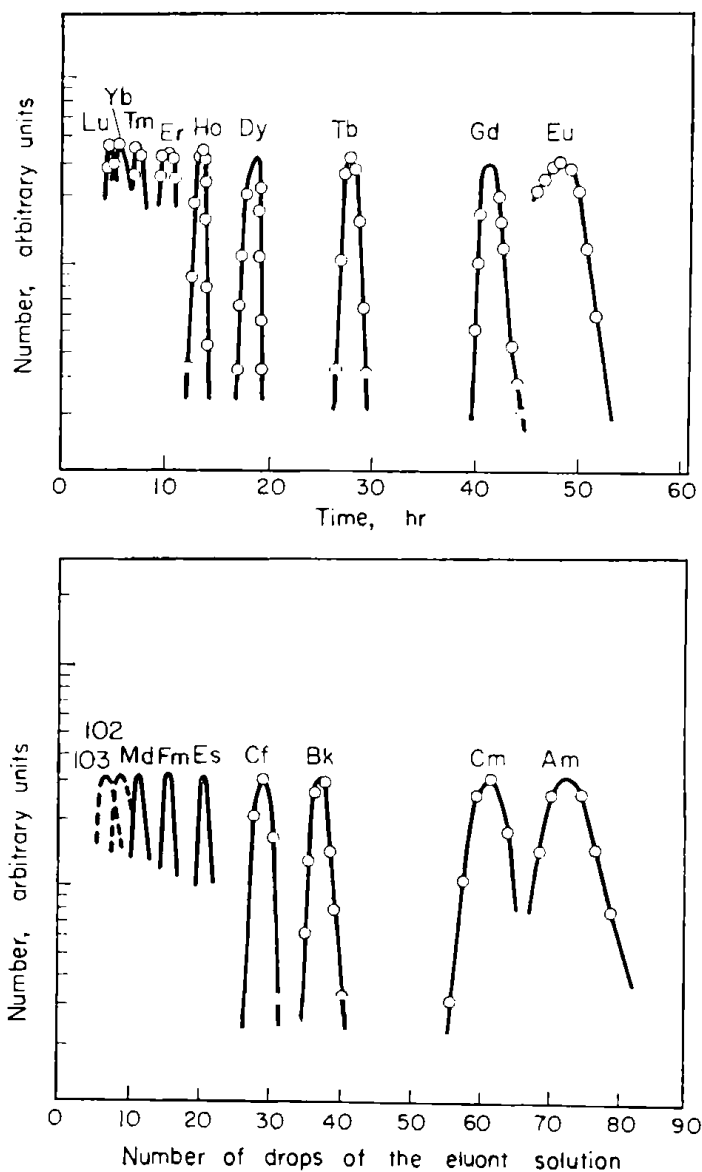


FIG. 21. Comparison of the elution curves of lanthanides (a) and actinides (b).

Wherein lies the similarity of the lanthanides with the actinides? Briefly in the following: the striking similarity in the absorption spectra, the existence of the so-called actinide contraction, similar to the lanthanide contraction, the shape of the curves of magnetic susceptibility; the presence of isomorphism between the different compounds of the actinides and the lanthanides; the position of the fractions in ion-exchange chromatography (see Fig. 21). Finally, comparison of the valency states of the elements indicates a certain similarity between the two families, although at the same time certain clearly marked differences in the chemical properties of the first few members of the family are also found.

TABLE 11  
*Comparison of the valencies of lanthanons and actinons*

Lanthanon	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Valency states	<b>3,4</b>	<b>3,4</b> ,(5)	<b>3</b> ,(4)	<b>3</b>	<b>2,3</b>	<b>2,3</b>	<b>3</b>	<b>3,4</b>	<b>3</b> ,[4]	<b>3</b>	<b>3</b>	<b>3</b> ,[2]	<b>3</b> ,2	<b>3</b>
	3,4	(3),4,5	3,4 5,6	3,4 5,6	3,4 5,6	(2),3 (4),5,6	3,4	3,4	3	[3]	[3]	[3]	[3],[2]	[3]
Actinons	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	102	103

In Table 11 the principal valencies are given in bold type. The possible valency states are given in round brackets and the proposed valencies in square brackets. As can be seen from the table, the first few elements of the actinide family have a far wider range of valencies than the first few lanthanides. The valency  $3+$  is by no means the principal valency in the Th–Pu series. It appears properly in americium only and becomes the principal valency in curium. This is explained as follows. The reader will remember that the  $4f$ - and  $5d$ -subshells are quite close to one another in their energy levels. As a result it is possible to use  $4f$ -electrons as valency electrons—hence the appearance of the quadrivalent state in cerium and praseodymium. The energies of the  $5f$ - and  $6d$ -subshells are still closer, so much so that it is rather difficult to distinguish between them, even if it is at all possible. For this reason the periphery of valencies for Th, Pa, U, Np, Pu and Am is considerably larger



than for their analogues in the lanthanide family. The tendency towards higher basic valencies is therefore expressed far less often. There is nothing surprising about the fact that there is no striking similarity between the first few actinides and lanthanides. Obviously careful study of derivatives with lower valencies in the Th-Am series should reveal much in common with the trivalent derivatives of the lanthanides. On the other hand, attempts to obtain lanthanide compounds in the valency state  $5+$ , and perhaps  $6+$  (theoretically excluded) may reveal similarities between compounds of actinides and lanthanides in a state of higher valency.

From curium onwards ( $Z = 96$ ) a complete similarity between the valency states of the elements of the two families is observed. It is remarkable that berkelium exhibits a valency of  $4+$  like its rare-earth analogue terbium.

In the final analysis the problem of allocation of the actinides in the periodic system may be solved not on the basis of precise evidence regarding the appearance of the first  $5f$ -electron alone. Incidentally, the presence of seven  $5f$ -electrons in curium and a structure similar to that of gadolinium are important pieces of evidence in favour of the actinide hypothesis. Chemistry also should have something important to say regarding the position of the actinides in the periodic table.

Until Rutherford's discovery of the process of artificial transformation of nuclei, chemists were concerned only with the electron shells of the atoms, and hence with properties due to the structure of these shells. Further achievements in science—the discovery of artificial radioactivity, the spontaneous fission of uranium, the construction of accelerators, which gave scientists a powerful tool for producing artificial radioactive isotopes—helped to create a new branch of chemistry, nuclear chemistry.

In the previous chapters we deliberately avoided the subject of natural and artificial radioisotopes of the rare-earth elements, the properties of their nuclei and problems concerning lanthanides, arising in connexion with advances in nuclear physics.

It is time we became acquainted with these topics.

### 3. Nuclear Chemistry of the Rare-earth Elements

The phenomenon of isotopicity among rare-earth elements began to be studied in the early 'thirties. Aston was the pioneer in this field. His first researches showed that lanthanum, praseodymium, terbium, holmium, thulium and lutetium have only one isotope each. Later he discovered two natural isotopes each for lanthanum and lutetium.

From then on the study of the isotopes of lanthanides proceeded in two directions. On the one hand there was the discovery of new natural isotopes—55 different types of atoms are known for the rare-earth elements at present. The other branch was the artificial production of the radioactive isotopes of these elements by means of various nuclear reactions. The list of “newly produced” lanthanide nuclei is even more encouraging and contains about 140 members. Their half-lives are spread over a wide range of values—from thousands of millions of years ( $\text{Sm}^{146}$  for example has  $T = 5 \times 10^7$  years) to a few minutes.

A study of this extensive material led scientists to many interesting conclusions. The chief of these is the proof of the existence of natural radioisotopes of the rare-earth elements. By itself there is nothing unusual about this fact. Natural radioactivity is characteristic of many elements of the periodic system, including elements with a low or medium atomic weight, such as carbon—14, potassium—40, calcium—41, rubidium—87, and some others. In all about 40 natural radioisotopes with long half-lives (from a few months to  $10^{21}$  years) are known today. Besides, more than 30 isotopes with a shorter lifetime have been discovered in the earth's crust.

If the radioactive elements at the end of the periodic system are considered, it will be found that their main characteristic is  $\alpha$ -decay, the emission of helium nuclei. Other forms of activity are observed to a lesser extent. These are ejections of an electron ( $\beta^-$ -decay), ejection of a positron ( $\beta^+$ -decay), and so-called orbital capture, in which the nucleus picks up an electron from any of the shells (in the case of the *K*-shell, the one nearest to the nucleus, the process is called *K*-capture). These modes of

conversion of nuclei are typical of light and medium radioactive isotopes mainly.

But the lanthanides have greater surprises in store for us. We shall begin by noting the anomalously large number of natural radioisotopes among the rare-earth elements. While there are only 13 natural isotopes with a long lifetime in the wide stretch from hydrogen to barium extending over 57 elements, at least nine out of the fifteen rare-earth elements have unstable natural modifications. The total number of radioisotopes of the lanthanides is at present eleven. We say "at present" because it is supposed, though not confirmed, that some other natural isotopes are also radioactive. On the other hand, there is the following very significant fact. Praseodymium, terbium, thulium and holmium all occur in nature in the form of one isotope only and these isotopes have been found to be radioactive. The two natural isotopes of lutetium have also been found to exhibit activity. It should be noted that these elements have an odd atomic number. Promethium, which has no stable isotopes, also has an odd atomic number ( $Z$ ). It may be supposed, therefore, that europium ( $Z = 63$ , two natural isotopes) is actually radioactive. Of the two isotopes of lanthanum one was found to be unstable. Thus "continuous" radioactivity may prove to be a common property of the odd lanthanides. On the whole, natural radioactivity has not yet been reliably discovered in only four out of the fifteen rare-earth elements—europium, gadolinium, erbium and ytterbium. This "burst" of radioactivity among the lanthanides deserves the most careful attention.

The natural radioisotopes of the rare-earth elements have, as can be seen from Table 12, a longer lifetime.

But another very interesting fact also emerges from this table.  $\beta$ -decay, which is "classical" for elements with a medium atomic weight, as the lanthanides are, was found in only three isotopes ( $\text{La}^{138}$ ,  $\text{Nd}^{150}$  and  $\text{La}^{176}$ ). All the others are  $\alpha$ -active.

None of the known radioisotopes had exhibited  $\alpha$ -decay before the rare-earth elements. It is true that scientists have succeeded in showing, on the basis of complex theoretical arguments, that lighter elements also are capable, in principle, of exhibiting  $\alpha$ -activity. The probability of this is, however,

TABLE 12

*Natural radioactive isotopes of the rare-earth elements*

Isotope	Type of decay	Half-life in years
La <sup>138</sup>	$\beta^+\gamma$	$3.2 \times 10^{11}$
Ce <sup>142</sup>	$\alpha$	$5 \times 10^{15}$
Pr <sup>141</sup>	$\alpha$	$>2 \times 10^{16}$
Nd <sup>144</sup>	$\alpha$	$5 \times 10^{15}$
Nd <sup>150</sup>	$\beta^-$	$>2 \times 10^{18}$
Sm <sup>147</sup>	$\alpha$	$6.7 \times 10^{11}$
Tm <sup>159</sup>	$\alpha$	$>5 \times 10^{16}$
Dy <sup>156</sup>	$\alpha$	$>10^{18}$
Ho <sup>165</sup>	$\alpha$	$>6 \times 10^{16}$
Tm <sup>169</sup>	$\alpha$	$>5 \times 10^{16}$
Lu <sup>175</sup>	$\alpha$	$>1 \times 10^{17}$
Lu <sup>176</sup>	$\beta^-$	$2.4 \times 10^{10}$

very small, because of the small decay energy and the very long lifetime. Lanthanides are situated at the boundary where the probability of  $\alpha$ -decay increases so much that it becomes possible, though difficult, to detect  $\alpha$ -activity in the rare-earth isotopes.

Some  $\alpha$ -active isotopes of the lanthanides have been produced artificially, e.g. Sm<sup>146</sup> ( $T = 5 \cdot 10^7$  years), Eu<sup>147</sup> ( $T \sim 24$  days), Gd<sup>148</sup>, Gd<sup>149</sup>, Gd<sup>150</sup>, Tb<sup>149</sup>, Tb<sup>151</sup> (the exact values for  $T$  have not been determined yet) and some others.

Thus the "burst" of radioactivity among the rare-earth elements is very characteristic—it is the first "burst" of  $\alpha$ -activity in the periodic system. The explanation for it lies in the nuclear structure.

Moving forward a bit we note that nuclei with 82 neutrons are distinguished by special properties. Theory shows that nuclei with about 82 neutrons have an increased tendency towards  $\alpha$ -decay. This is particularly true of nuclei with 84 neutrons. By ejecting an  $\alpha$ -particle (consisting, as we know, of 2 protons and 2 neutrons) these are transformed into stable 82-neutron nuclei. In the language of nuclear physics, the rare-

earth elements are situated in just that region where the shell of 82 neutrons appears.

Table 13 gives the number of isotopes of the rare-earth elements.

TABLE 13  
*Number of isotopes of the rare-earth elements*

Serial Number	Element	Number of natural isotopes	Number of artificial isotopes
57	Lanthanum	2	12
58	Cerium	4	10
59	Praseodymium	1	11
60	Neodymium	7	7
61	Promethium	?	14
62	Samarium	7	10
63	Europium	2	14
64	Gadolinium	7	10
65	Terbium	1	9
66	Dysprosium	7	6
67	Holmium	1	8
68	Erbium	6	7
69	Thulium	1	7
70	Ytterbium	7	5
71	Lutetium	2	8

It can be easily seen that rare-earth elements with an even atomic number have considerably more natural isotopes as against the elements with an odd atomic number which have one or two. Thus even in the family of the rare-earth elements the general rule, that elements with even  $Z$  have more stable isotopes, than those with odd nuclear charge, is found to be true. This rule is related to the abundance of the rare-earth elements: those with even atomic number are considerably more abundant.

The ratio of the total abundance of the rare-earth elements with an even to those with an odd atomic number is approximately 6. This is also the ratio of the average number of isotopes of the 2 varieties.

The number of radioactive isotopes of the rare-earth elements produced artificially is very great. It is worth noting that for promethium, not yet discovered on the earth's crust, no less than 14 radioisotopes have been produced artificially—a brilliant example of the progress achieved in nuclear physics.

Artificial isotopes of the rare-earth elements are obtained with the help of nuclear reactions. It will be remembered that this term indicates a process involving bombardment of the atomic nuclei of an element by particles of different energies (protons, nuclei of heavy hydrogen,  $\alpha$ -particles, neutrons) or irradiation with  $\gamma$ -rays. Thus, Rutherford, who was the first to carry out artificial conversion of elements, subjected nitrogen nuclei to the action of  $\alpha$ -particles.

As a result a proton escaped from the compound nucleus formed and the nucleus of an oxygen isotope, another chemical element, was obtained. This nuclear reaction is written as  ${}_7\text{N}^{14} + {}_2\text{He}^4 \rightarrow {}_1\text{H}^1 + {}_8\text{O}^{17}$ , or in an abbreviated form,  ${}_7\text{N}^{14}(\alpha, p){}_8\text{O}^{17}$ .

Artificial isotopes of all the rare-earth elements can be obtained with the help of various nuclear reactions. The natural isotopes can also be transformed by this means.

The terbium isotope  $\text{Tb}^{160}$  can be obtained in two ways: irradiation of  $\text{Tb}^{159}$  with neutrons or  $\text{Gd}^{160}$  with the nuclei of heavy hydrogen. The nuclear reactions which occur are  $\text{Tb}^{169}(n, \gamma)\text{Tb}^{160}$ , and  $\text{Gd}^{160}(d, 2n)\text{Tb}^{160}$ .  $\text{Tm}^{177}$ , which is already known to us, is formed as a result of the nuclear reaction  $\text{Tm}^{169}(n, \gamma)\text{Tm}^{170}$ .

Nuclear reactions in which the bombarding particles are neutrons are the easiest to bring about. As is well known, the neutron has no charge and hence the energy barrier does not present any obstacle to its penetration. These reactions are also the most important in practice. The well-known fission reaction of uranium, which forms the basis of the production of atomic energy, is based on the action of neutrons. Nuclear reactions are divided into slow-neutron and fast-neutron reactions depending on the energy of the escaping neutrons.

It should not be thought, however, that nuclear reactions can be carried out with the same ease with the atomic nuclei of any element. In some cases the nuclear transformations occur

quickly and simply; in others the probability of a nuclear reaction is small. The so-called capture cross-section ( $\sigma$ ) is used to express quantitatively the probability of any process of nuclear transformation. This quantity has the dimensions of an area and is measured in centimetres or barns (1 barn corresponds to  $10^{-24}$  cm<sup>2</sup>). The greater the capture cross-section the greater is the probability of a given nuclear reaction.

A remarkable characteristic of the rare-earth elements is the anomalously large values of the capture cross-section. In some lanthanides it is greater than in all the other elements. Thus samarium, europium and gadolinium have cross-sections equal to 6500, 4500 and 44,000 barns respectively, which are very much greater than the values for cadmium (2500 barns) and boron (3000 barns)—elements considered “classical” in this respect. These properties of the rare-earth elements make it possible to use them for the preparation of regulating rods in nuclear reactors. On the other hand, even an insignificant admixture of the rare-earth elements in the fissile materials (i.e. materials which are nuclear fuels) can sharply reduce the efficiency of a fission reaction. Careful purification of thorium, uranium and plutonium from possible “rare-earth” contaminations is therefore a necessary stage in the technology of these metals.

The use of nuclear reactions is only one of the methods of preparation of isotopes of the rare-earth elements. Another method is their extraction from fission fragments of uranium in the nuclear reactor. As is well known, during the fission reaction the uranium nucleus breaks up into two fragments which are nuclei of elements from the centre of the periodic system.

Rare-earth elements form a considerable portion of these fragments (in some cases up to 30 per cent). It was from these products of the fission of  $U^{235}$  by slow neutrons that two isotopes of the “elusive sixty-first” promethium,  $Pm^{147}$  and  $Pm^{149}$ , were first obtained. It was shown that the yield of these isotopes during fission amounts to 2.6 and 1.3 per cent, respectively.

The fact that about 1.5 g of promethium is obtained in only 24 hr as a result of the operation of a reactor of average capacity shows how promising is the method of obtaining iso-

topes of the rare-earth elements from the fission products of uranium.

The use of radioactive isotopes in science, technology and agriculture is increasing rapidly. The use of radioisotopes of the rare-earth elements is still in its infancy but even the first steps taken in this direction suggest that many new and unexpected fields of application will be discovered in the near future. But an examination of the radioactive and other properties of the isotopes of lanthanum and the lanthanides is of considerable interest from another aspect also—the theoretical aspect. More than 1400 isotopes of all the elements are known at present. Of these 70 per cent belong to the rare-earth isotopes. This raises the question of establishing a systematic scheme of atomic nuclei.

#### 4. Another Periodic System

Classical chemistry is concerned mainly with the electron shells of atoms, and more specifically with the outer electron shells, since it is these which determine the chemical properties of the elements. The fundamental law of classical chemistry—Mendeleev's periodic system—introduced a rigorous order into the vast variety of properties of the 102 elements by establishing a periodic variation of the properties with increase in the serial number, i.e. the nuclear charge.

But nuclear chemistry, the chemistry of atomic nuclei, cannot be satisfied with the periodic table, although this table forms its theoretical basis by determining the possible methods of transformation of the elements. On the basis of the periodic system alone it is impossible to predict the existence of new isotopes, not yet obtained, and to describe their properties or establish a relation between them. Finally, the periodic system cannot accurately describe the nature of the variation in a whole series of properties which depend on the structure of their nuclei.

Hence it is necessary to take a step forward. One must consider the existence of regularities in the properties of atomic nuclei. Is there not a certain periodicity in these properties? In other words a systematic scheme of atomic nuclei has to be assembled.



At present we are concerned only with the outlines of a theory which may be made elegant in future. Naturally one should not rely blindly on Mendeleev's periodic system. The periodicity in the properties of atomic nuclei should not be identified with the periodicity in properties connected with the electron shells. The forces acting in the nucleus are qualitatively different from those in the electron shells. But the idea of the existence of particularly stable nuclear structures (similar to the stable electron shells of inert gases) should be used in drawing up a systematic scheme of atomic nuclei.

From numerous investigations it is possible to arrive at the conclusion that special proton and neutron shells exist in the nuclei. Nuclei with the number of neutrons and protons equal to 2, 8, 20, 50 or 126, corresponding to completed shells, have the most stable structures. In addition to the closed shells, subshells containing 14, 28, 64, 96 and 152 protons or neutrons were also discovered. It is not impossible that in nuclear structure they play a role similar to that of the electron subshells in atoms.

At the moment a variant of the "periodic system" of atomic nuclei can be proposed in which, for example, there are seven periods ending with the following nuclei:  $\text{He}^4$  ( $2p, 2n$ ),  $\text{O}^{16}$  ( $8p, 8n$ ),  $\text{Ca}^{40}$  ( $20p, 20n$ ),  $\text{Zr}^{90}$  ( $40p, 50n$ ),  $\text{Sn}^{119}$  ( $50p, 69n$ ),  $\text{La}^{139}$  ( $57p, 82n$ ),  $\text{Pb}^{208}$  ( $82p, 126n$ ). Then comes the eighth period, as yet incomplete. These nuclei apparently play the role of a kind of "inert gas". The presence of a stable structure in them is reflected in many properties, in particular in the values of the absolute abundance of these in nature. In the rare-earth elements, for example, there is a considerable increase in the content of isotopes with 82 neutrons: for  $\text{Nd}^{142}$  the abundance is 5 times larger than that of the mean abundance of the rare-earth elements, for  $\text{Pr}^{141}$ —8 times, for  $\text{Ce}^{140}$ —12 times and for  $\text{La}^{139}$ —27 times.

It is of course too early to speak of the system of atomic nuclei as something fixed and definite. Its development depends on further progress in nuclear physics and the clarification of obscure questions.

But even in its present state the system can be used in practice, in particular for predicting the stability of nuclei to disintegration or spontaneous fission.

The special features of nuclear properties of rare-earth elements are still far from being studied properly. But it need not be doubted that the future "periodic system" will explain the many qualities peculiar to the nuclei of the isotopes of the rare-earth elements like the capacity for  $\alpha$ -disintegration, the relatively large number of natural radioisotopes, the anomalously large values of the capture cross-section and finally, the magnetic properties. The peculiar nature of this strange family of elements will thus again be emphasized.

### 5. Does Promethium Exist in Nature?

Fourteen isotopes of promethium have been obtained up till now. Of these the ones with the longest lifetimes are  $\text{Pm}^{145}$  ( $T \sim 30$  years),  $\text{Pm}^{147}$  ( $T = 2.7$  years) and  $\text{Pm}^{146}$  ( $T = 2$  years). Most of the isotopes of Pm disintegrate by emitting a  $\beta^-$ -particle. This type of activity is observed beginning with  $\text{Pm}^{146}$ , and is in conformity with the general rule that nuclei with an excess of neutrons, i.e., heavy isotopes of an element, are subjected to  $\beta^-$ -decay. The essence of  $\beta^-$ -decay lies in the transformation of neutron into a proton. The characteristic properties of the light isotopes of promethium are emission of a positron and K-capture—forms of activity typical of light isotopes of elements with a deficiency of neutrons.

The study of the properties of the "elusive" element 61 began immediately after the element had been separated in appreciable quantities. In 1948 the American scientists Parker and Lanz prepared 3 mg each of a yellow chloride  $\text{PmCl}$  and a pink nitrate  $\text{Pm}(\text{NO}_3)_3$ . Careful chemical investigation showed, as was to be expected, that anomalous valency states ( $2+$  and  $4+$ ) are not characteristic of promethium. Situated as it is in the middle of the cerium group, the element is not inclined to exhibit a valency other than 3. Scientists were able to investigate the atomic spectrum of promethium, its isotope  $\text{Pm}^{147}$ , obtained by the fission of  $\text{U}^{235}$  by slow neutrons. The idea suggested itself that this spectrum be compared with those on the basis of which investigators had previously announced the discovery of element 61.

The comparison gave a negative result. Thus the whole

previous history of the “elusive” element 61, although very complicated and instructive, turned out to be a history of errors and misunderstandings. The methods of spectra analysis had been responsible for the “discovery” of element 61 more than once. It seemed they were destined to give a categorically negative answer to the question of the existence of promethium in nature.

And yet this question retains its interest for theory.

The fact that promethium does not have stable isotopes does not mean that the element cannot have isotopes with long lifetimes. But the artificial production of fourteen isotopes of the element showed that the most “honoured” of these, Pm, was 30 years old.

The isotope  $\text{Pm}^{145}$  decays by emitting a positron and is transformed into  $\text{Nd}^{145}$ . The half-life is 30 years and determines the degree of instability of  $\text{Pm}^{145}$  for this type of decay. As we know already, there is a burst of radioactivity in the series of rare-earth elements. The probability of  $\alpha$ -decay increases considerably for isotopes containing 84 neutrons. Theoretical calculations show that the energy of  $\alpha$ -decay of  $\text{Pm}^{145}$  should be 2.3 MeV and its half-life will be  $10^{11}$ – $10^{12}$  years. Such a lifetime is much longer than the period of existence of the earth.

In the case of  $\text{Pm}^{145}$  we find a so-called radioactive “fork”, when an isotope can decay in two ways:  $\beta^+$ -radiation and emission of  $\alpha$ -particles. This phenomenon is not rare among radioactive isotopes.

The second possibility of discovering promethium in nature consists in the process of spontaneous fission of  $\text{U}^{238}$ . Radioisotopes of many chemical elements, including  $\text{Pm}^{147}$ , are formed as a result of this. The half-life of this isotope is 2.7 years and is sufficient for the separation of  $\text{Pm}^{147}$  from a complex mixture of fission fragments of  $\text{U}^{238}$  that is difficult to separate. The difficulty lies in the fact that the isotope occurs in vanishingly small quantities in the earth’s crust. Scientists have calculated that during the period of existence of the earth  $10^{-15}$  g of  $\text{Pm}^{147}$  have been formed in all for every 100 g of uranium. The methods available do not allow detecting such negligible amounts of an element at present.

The next method of formation of promethium in nature is

by the  $\beta^-$ -decay of  $\text{Nd}^{150}$ . But the  $\text{Pm}^{150}$  thus formed has a very short half-life ( $\sim 2.7$  hr). The isotope decays completely during the time spent in separating the lanthanides.

Fourthly and lastly, promethium can be formed as a result of numerous nuclear reactions occurring in nature. No definite evidence is available yet but investigations in the near future are sure to give a final answer.

## 6. The Origin of the Elements

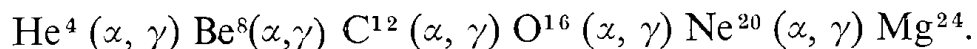
There is one problem which is still in the initial stages of investigation and the rare-earth elements may play no insignificant role in its solution. This is the problem of the origin of the elements.

We can only touch upon this problem here.

We shall have to begin with systems where the temperatures and pressures prevailing are difficult to imagine—systems where all the conditions for the occurrence of numerous nuclear reactions leading to the transformation of elements are present. The stars are such systems.

It was established fairly long ago that the main source of the energy of the stars is the conversion of hydrogen into helium. This transformation can occur in different ways, each peculiar to a definite stage of evolution of the stars.

In course of time hydrogen is burnt out and at the same time helium accumulates. The enormously high temperatures (tens of millions of degrees) and pressures (hundreds of millions of atmospheres) in the stars make it possible for the helium nuclei to fuse with each other and form the heavier elements of the beginning of the periodic system. The following series of transformations may serve as an example:



The presence of hydrogen atoms—free protons—can continue this chain in the direction of the formation of elements with a higher nuclear charge, due to the  $(p, \gamma)$  reaction. For example,  $\text{Ne}^{20} (p, \gamma) \text{Na}^{21} (p, \gamma) \text{Mg}^{22}$ , etc.

But as the hydrogen is burnt out, the probability of nuclear reactions involving the capture of protons is reduced and

reactions accompanied by the capture of an  $\alpha$ -particle and the emission of a neutron, e.g.  $\text{Ne}^{21}(\alpha, n)\text{Mg}^{24}$ , step into the foreground. Thus a large number of free neutrons are produced in the interior of the stars and this makes the formation of heavy elements according to  $(n, \gamma)$  reactions possible. Indirect evidence for the occurrence of such processes is provided, for example, by the detection of lines corresponding to the element with  $Z = 43$ , technetium, in the spectra of some stars, including the sun. As is known, this element has not been discovered on the earth's surface due to the instability of its isotopes. But the half-life of the longest lived technetium isotope is 216,000 years. This means that the element was synthesized in the process of evolution of the stars, which extends over a considerably longer period. Apparently the formation of elements heavier than technetium from  $(n, \gamma)$  reactions is also possible.

But subsequently a limiting factor becomes operative. For, as the nuclei become more complex the probability of the emission of  $\alpha$ -particles, i.e. the  $\alpha$ -disintegration of nuclei, increases. The formation of elements of the second half of the periodic system and particularly those at the end of the system, from the  $(n, \gamma)$  reaction is therefore unusual. Temperatures of the order of 50 million degrees in the interior of the stars cannot also guarantee the occurrence of thermonuclear reactions on the basis of elements heavier than hydrogen, such as oxygen or nitrogen, as they cannot ensure the appearance of a large flux of neutrons in a short interval of time. For this higher temperatures of the order of  $10^{10}$  degrees are necessary.

Such temperatures can be attained only during the explosion of what are called supernovae. They are produced as a result of the disturbance in solar systems caused by a difference in temperature between the core of the star and the film surrounding it. This in its turn is explained by the different types of nuclear processes occurring in the core and the film at a late stage of evolution of the star. During the explosion of a supernova enormous quantities of matter are thrown out into space and the remainder is compressed. This is accompanied by a sharp rise in temperature which helps a very intense nuclear activity. This again leads to a very powerful flux of neutrons in a very short time (up to 10 sec).

Thus conditions are established for the successive addition of neutrons to the nuclei of elements. This can lead to the formation of the heaviest elements, right up to californium,  $Z = 98$ .

But there are limiting factors for this process also. First of all there is the instability of the nuclei of the heavy elements to  $\alpha$ -disintegration. Secondly, the probability of the process of spontaneous fission increases for the heaviest elements. In particular, it was proved that the energy emitted by supernovae after explosion is due to the kinetic energy of the fragments of spontaneous fission of the nuclei of the californium isotope  $\text{Cf}^{254}$ , which has a half-life of 55 days.

The existing theories of the origin of the elements are still full of unsolved problems and are at times contradictory. It is too early to speak of a single comprehensive theory. The fact is that, until recently, a strictly theoretical approach alone was possible to the processes occurring in the interior of the stars.

It is only in the past decade that scientists have had at their disposal laboratories in which problems connected with the origin of the elements could be posed and solved in practice.

First, there were the advances in nuclear physics which made it possible to produce artificially 10 elements heavier than uranium. These elements were unknown in the conditions of the earth's surface. A practical shape was thus given to the processes of transformation of elements by the synthesis of radioactive isotopes. Secondly, people were able to realize, under terrestrial conditions an instantaneous thermonuclear reaction, similar to those occurring in the interior of the stars, and thus proceed directly to the solution of the problem of controlled thermonuclear reactions. Lastly, there were the investigations on cosmic rays and nuclear reactions occurring on the earth's surface.

Naturally the question arises, what is the relation between the problem of the origin of the elements and the family of rare-earth elements. It is of course impossible at present to point to any direct connexion but a number of considerations impel us to examine the rare-earth elements very thoroughly in this respect also.

It has been pointed out already that the capacity of elements for  $\alpha$ -disintegration becomes apparent only from the rare-earth

elements. Not a single isotope, natural or artificial, is subject to  $\alpha$ -disintegration before this family. On the other hand, as a result of disintegration produced by neutrons or of spontaneous fission of the elements at the end of the periodic system, the fragments formed contain a considerable portion of rare-earth elements. Thus the family of rare-earth elements possibly forms a peculiar intermediate group from the point of view of their origin also. It seems they can be formed in two ways: (1) from the  $(n, \gamma)$  reaction in the stages of calm during the evolution of the stars and the explosion of supernovae and (2) as a result of the spontaneous fission of the very heavy elements after the explosion of supernovae.

But the solution of this problem has to be left to the future.

## CONCLUSION

IN relating the history of the discovery of rare-earth elements and their distribution in the periodic system we looked back at the past. By touching on the practical applications of lanthanum and the lanthanides we emphasized the importance of these elements in our age. We can therefore now say a few words in conclusion on the future of the fifteen elements.

It should be emphasized immediately that in this age of unprecedented progress of science and technology our knowledge about the rare-earth elements is inadequate. It does not correspond to the present state of development of chemistry and physics although in the last 10–15 years scientists have discovered a number of new facts about the properties of the rare-earth metals and their compounds. The fields of application of these subjects have been considerably extended. More and more branches of industry are using the rare-earth elements. Nobody doubts any longer that lanthanum and the lanthanides have a great future.

But two factors prevent extending the range of application of the rare-earth elements.

The first factor is the high cost of pure preparations of the rare-earth metals and their compounds. In the U.S.A., for example, 1 kg of gadolinium oxide (99 per cent pure) costs up to 600 dollars, and of ytterbium oxide up to 900 dollars and of holmium oxide up to 700 dollars. The pure metals are even more costly. If we consider the price of gold (1100 dollars per kg), it is obvious that the price of rare-earth preparations are much higher and they cannot be used to the proper extent in industry.\*

\*The prices given in the original manuscript were  $\text{Gd}_2\text{O}_3$ : \$6000 per kg,  $\text{Yb}_2\text{O}_3$ : \$25,000, and  $\text{Ho}_2\text{O}_3$ : \$350,000. These figures have been corrected. It is not felt completely correct to suggest also that the price of rare-earth



The second factor is the insufficient extent to which the properties of the rare-earth elements have been studied. This also retards their practical application. The properties of cerium have been studied more closely than those of the others and it is quite natural that this element should have a very wide range of application. But in order to study the properties of an element thoroughly it should be available in sufficient quantities and in as pure a state as possible.

There is enough rare-earth raw material on the earth. The deposits are sufficient to meet any industrial demands. The problem consists in making the production of rare-earth elements as cheap as possible.

One does not have to be an economist in order to understand that the processes of separation of these elements and their isolation in the pure state form the main portion of the expenses.

Unfortunately even the most advanced methods are not universally applicable, ones which would make it possible to separate the different rare-earth elements in a highly pure state on an industrial scale, simply, quickly and reliably. The most promising methods are those of ion-exchange chromatography and separation on the basis of variable valencies. These have not been sufficiently developed yet.

And all this is because our knowledge of the chemistry of the different rare-earth elements leaves much to be desired. First of all there are the anomalous valencies: the conditions of their appearance, the properties of the compounds in which the valencies of the rare-earth elements differ from  $3+$  are imperfectly known. Something is known about  $\text{Ce}^{4+}$ ,  $\text{Sm}^{2+}$  and  $\text{Yb}^{2+}$ , but there is very little data on quadrivalent terbium and praseodymium, bivalent europium and possibly thulium. The question of obtaining the remaining lanthanides in a state of anomalous valency is still open.

Determination of the conditions in which rare-earth elements might exhibit variable valencies and the ability to make use of these conditions would give the scientist a simple and rapid method. The price of rare-earth metals is higher than that of gold—gadolinium metal for example is selling in U.S.A. for \$300 per lb or ~\$660 per kg. Prices for other rare-earth metals depend greatly upon the individual metal and many of these are being consumed in quantities of up to several hundreds of lb/year.

method of separating the rare-earth elements. For the main difficulty would then be overcome—the similarity of the properties in the valency state  $3+$ .

The solution of the problem of anomalous valencies would be important not only from the practical point of view. It is of theoretical interest also. By comparing the conditions of appearance of the different valencies in the lanthanides and actinides it would be possible to look for more important similarities between the elements of these families and thus obtain a final solution of the problem of the position of the actinides in the periodic system.

A thorough study of the individual elements is one of the principal problems of the chemistry of rare-earth elements. It cannot be disputed that new, unexpected ways of using the rare-earth elements will be discovered in the near future. But without indulging in fantasy it is possible to point out some of the fields in which the application of rare-earth elements has a great future.

First of all comes metallurgy. The favourable effect of admixtures of rare-earth metals of the cerium group in alloys of magnesium and aluminium and to steels of various types has already been demonstrated. But the effect of the “heavy lanthanides” is still unknown. Naturally alloys in which the rare-earth elements will form the chief components (or one of the chief components) instead of playing a subordinate role will be of great interest. Finally, the study of systems formed by the individual lanthanides with one another should lead to a number of new discoveries.

Another field is that of the investigation of the catalytic action of the rare-earth elements. The first results obtained are encouraging. The extensive application of lanthanides as catalysts and promoters will not only prove valuable in practice but will also help to solve an important theoretical problem—the selection of catalysts. The study of the catalytic action of compounds of the rare-earth elements on polymerization processes is of great interest. In this connexion investigation of the possibility of obtaining metallo-organic compounds of the lanthanides is important.

The super-conductivity of lanthanum, and possibly the other

lanthanides, the unique magnetic properties and the extraordinarily large capture cross-sections of some rare-earth elements, the ferro-magnetism of gadolinium and dysprosium—these are the properties which will also help an extensive use of the rare-earth elements.

Atomic batteries with  $\text{Pm}^{147}$  and X-ray equipment using  $\text{Tm}^{170}$  as a source of radiation—these are only the first practical applications of the radioisotopes of the lanthanides. It cannot be doubted that great advances will be made in this field also. We have already mentioned how important is the study of the nuclear chemistry of the rare-earth elements. Evidence for the methods of their formation is an important link in the solution of the general problem of the origin of the elements.

“Rare-earth elements are a forgotten branch of inorganic chemistry”—it used to be said a few decades ago. We have quoted these words at the beginning of this book. We are quoting them here again in order to emphasize once more that a scientific problem that appears fruitless at first sight sometimes proves to be unusually promising and have various applications and radically alters established opinion. It would not be surprising if in the near future the rare-earth metals become just as common in science and industry as, for example, magnesium or aluminium are now.

## NOTES

1. For further particulars on this see Chapter 5.
2. Incidentally, even Lavoisier supposed that these “earths” were not elements but rather oxides.
3. Berzelius and Hisinger reached this conclusion almost simultaneously.
4. It should be borne in mind that the name “rare earths” corresponded to oxides of metals in the early stages of their discovery and study. We therefore imply oxide of the element when we speak of an “element”. These elements were obtained in the metallic state at the end of the 19th century and some of them considerably later.
5. The names are derived from Ytterby.
6. As a matter of historical interest it may be noted that for a number of reasons there was some confusion in the names. Mosander’s erbia began to be called terbia, and terbia was called erbia.
7. See, for example, *Principles of Chemistry*, 3rd ed. 1877.
8. At the beginning of the 20th century the atom was considered as a sphere charged with positive electricity, with negative charges—electrons—distributed uniformly over its volume.
9. In the course of later developments in atomic physics it became clear that the concept of definite electron orbits is an over-simplified one. This gave rise to the concept of a number of shells in which the electrons surrounding the nucleus are situated.
10. It can now be understood that Bohr’s theory leads to the unambiguous conclusion: hafnium cannot belong to the lanthanide family.
11. According to present-day data, there are *5d*-electrons in Gd, La and Lu.

12. The question of the boundary between the cerium and yttrium groups is of great theoretical importance. Even some specialists and practical chemists do not have a very clear idea of it. It is therefore worthwhile dwelling on it in some detail. The division into groups was at first based on the discovery of the elements concerned in different minerals. Later, as methods of analysis were improved, it was shown that this principle was inadequate as a basis of classification. Yttrium "earths" were discovered in "classical" cerium minerals and vice versa. Gradually a more extensive and deeper knowledge of the properties of the rare-earth elements was gained. Almost the only universal method of separation in those days was that of fractional crystallization and to apply it knowledge of the solubilities of the various compounds was absolutely essential. The solubility data formed the new basis of classification. But on the other hand, they introduced unimaginable confusion, some of which we find even to-day. The majority of the compounds used for the division of the rare-earth elements into groups (sulphates, carbonates, formates of the alkali metals) formed, as was thought then, "double salts" with different solubilities in water. Later it was shown, that in this case the different solubilities are found not only and not so much in water as in an excess of a precipitating agent, i.e., complex-formation takes place. In the rare-earth elements the capacity for complex-formation increases gradually and almost continuously with increase in the serial number. In other words, whether any of the rare-earth elements will remain in the precipitate or pass into the solution wholly or partly depends on the amount of the precipitating agent, i.e. an investigator may, within certain limits, relate a certain element, particularly one of the controversial "transition" elements, to the cerium or yttrium group at will. Naturally such a "criterion" cannot stand up against criticism. It is therefore impossible to devise a system of subdivision into groups on the basis of purely chemical characteristics; it has to be based only on a knowledge of the structure of the electronic configuration of the rare-earth elements, i.e. on physical data. These data very clearly indicate the presence of a boundary between gadolinium and terbium. Discussion about the boundary is by no means an abstract

question. For, besides properties changing continuously over the whole family, there are those that change periodically and a correct arrangement of the rare-earth elements in two groups even makes it possible to predict some properties of the analogue elements. Thus, on the basis of an arrangement of atoms similar to the arrangement of the ions in Fig. 5, V. Klemm predicted the existence of a bivalent state for ytterbium on the analogy of the properties of its analogue in the cerium group—europium. Ytterbium was subsequently reduced to this state in practice.—*Ed.*

13. Quadrivalent cerium does in fact give a number of very stable compounds. For example, cerium dioxide  $\text{CeO}_2$  is the usual gravimetric form of the compounds of both  $\text{Ce}^{4+}$  as well as  $\text{Ce}^{3+}$  obtained on calcination. The oxidation of colourless  $\text{Ce}(\text{OH})_3$  by the oxygen in the air into the yellow hydroxide of quadrivalent cerium proceeds gradually even at room temperature.

A number of salts of  $\text{Ce}^{4+}$ , are also known, which are stable in aqueous solutions (sulphate, nitrate and some others). For praseodymium, on the other hand, neither aqueous solutions of salts with the cation  $\text{Pr}^{4+}$  nor the hydroxide of quadrivalent praseodymium are known yet. The only compound in which the highest valency of this element can be considered as definitely established is the oxide with the empirical formula  $\text{Pr}_6\text{O}_{11}$ .

— *Ed.*

14. The ionic radii according to V. M. Goldschmidt and L. Pauling (1926–27) are given in Table 4. In 1954 the eminent crystallographer V. Zachariasen calculated the exact values of the radii of  $\text{Me}^{3+}$  for the lanthanides on the basis of experimental data. These values are:

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy
1.04	1.02	1.00	0.99	(0.98)	0.97	0.96	0.94	0.92	0.91
			Er	Ho	Tm	Yb	Lu		
			0.89	0.87	0.86	0.85	0.84		

As can be seen, in Zachariasen's values the continuity in the variation of  $r_{\text{Me}^{3+}}$  is practically undisturbed and no anomalies are observed, such as those inherent in Goldschmidt and Pauling's series.

15. It is interesting to note that rare-earth elements are constantly present in soils, plants and animal organisms. Thus about 0.02 per cent of these elements have been observed in soils and 0.002–0.0051 per cent in plant ashes. The highest concentration was found in lupin and sugar beet.

The rare-earth elements definitely exert an influence on the growth and development of plants but the nature of this is not yet clear. The part played by them in animal organisms has not been studied at all, although there are indications that they shew special affinity for the bones.

16. In certain cases there is a two-electron configuration (Li, Be, B, Y).

17. The isomorphic mixtures mentioned above are, according to present-day ideas, solid solutions. The homogeneity of the solid solution is not destroyed on varying the proportions of its components. The possibility of isomorphic substitution when there is one common anion and all the cations are of the same valency is determined only by the degree of proximity in size between these cations. The data given in Table 4 explain the possibility of the formation of mixed crystals by the lanthanide compounds of the same name. These elements are usually trivalent under normal conditions; the difference in the values of the ionic radii for the first and the last members of the cerium group is 0.11 and 0.10 for the yttrium group. It does not exceed 0.4 Å on passing from one element to another inside the groups. In geochemistry there is an empirical rule according to which isomorphic substitution is possible (all other conditions being observed) if the ionic radii of two elements do not differ by more than 15 per cent of the radius of the smaller ion. It can be easily verified that this rule is observed for the elements of the two groups. Because of this, the majority of the compounds of elements of one and the same group are crystallized in one system and isomorphously between themselves in a large range of proportions of the different components. For this reason yttrium does not form independent minerals but is found only in those minerals which contain the yttrium group. This is why all the elements of each group are found together in minerals. One cannot however speak of an unlimited solubility of the compounds of all the lanthanides as

a consequence of the law mentioned above, because in extreme cases the differences in ionic radii exceed the admissible limit and this leads to different crystalline forms for elements of the cerium and yttrium groups. For example, the orthophosphates of the elements of the cerium and yttrium groups form two minerals under natural conditions—monoclinic monazite and tetragonal xenotime respectively.—*Ed.*

18. According to their magnetic properties, all substances can be divided into diamagnetic (magnetic susceptibility  $\kappa$  = less than zero), which are repelled by the pole of a magnet, and paramagnetic ( $\kappa > 0$ ), those attracted by a magnet. Substances with a very strongly marked paramagnetism are called ferro-magnetic ( $\kappa$  is large).

19. Basic fractional precipitation, like fractional crystallization, is called a fractional method because of the technique used. A schematic diagram of the process of basic fractional precipitation is very similar to the “tree of crystallization”. In both methods separation is based on making use of slight differences in the corresponding properties and amounts in practice to multiple repetition of operations of the same type.

But while comparing these two methods, externally very similar, it should be noted that the elementary act of separation in the process of fractional crystallization can be carried out considerably more simply and quickly than in the case of basic precipitation. It is therefore convenient to use it only in those cases when the enrichment factor of a particular precipitating operation considerably exceeds that of a single recrystallization. The main drawback of the method consists however in the following fact: Although the basicity varies gradually with  $Z$  and is very marked for members of the family far apart from one another, this difference is so small for some neighbouring elements that similar “pairs” (e.g. Pr–Nd) cannot be separated.—*Ed.*

20. Amalgams of Sm, Eu and Yb can be obtained from mixed acetate–citrate solutions either with the help of an exchange reaction with an amalgam of an alkali metal or by electrolysis with a mercury cathode. In both cases, the ytterbium amalgam formed (if the mixture of elements of the yttrium group is subjected to reduction) or a mixture of Sm and Yb (if the



material contains the cerium group) is separated from the initial solution and then subjected to acidic decomposition. The preparation of ytterbium thus obtained is spectroscopically pure. The mixture of Sm and Yb, free from impurities of other rare-earth elements, is subjected to further separation. In the methods described Sm, Eu and Yb are subjected to thorough reduction (to the metallic state).

The method of electrolytic reduction of mixtures in the presence of sulphate ions is also used. In this case Eu and Yb are reduced only to the bivalent state, difficult soluble precipitates of  $\text{EuSO}_4$  or  $\text{YbSO}_4$  are formed and these are separated from the mother liquor and mercury. Preparations of a very high degree of purity cannot be obtained with this method because of contamination of the precipitates formed with the mother liquor.—*Ed.*

21. We shall not give a detailed description of the chromatographic method. The reader can learn about it from the extensive literature, both for the specialist and the layman, on ion-exchange chromatography.

## INDEX

- Abundance of rare-earth elements 47-51
- Actinides 96-100
- Aldebaranum, discovery of 11
- Anomalous valencies 38-40
- Applications of the rare-earth elements 73
  - in archeology 89
  - in chemical industries 79, 80
  - in electrical devices 90, 91
  - in ferrous metallurgy 76-9
  - in medicine 89
  - in nuclear technology 91
  - in separation of transuranic elements 87
- Bohr's prediction of the existence of a family of elements similar to rare earths 96, 97
- Bohr's theory 15, 27
  - and application to periodic law 28, 33
- Cassiopeium, discovery of 11
- Ceria, occurrence of 3, 4
- Cerium 21
  - group electronic structure 37
- Chemical characteristics of rare-earth elements 57, 62
- Definitions of rare earths 3
- Didymium, discovery of 5
- Discovery of the rare-earth elements 1-11
- Dysprosium, discovery of 11
- Effect of additions of rare-earth metals on the mechanical properties of magnesium alloys 78
- Effect of cerium oxide on the resistance of glass to  $\beta$  radiation 82-3
- Electrical properties 54
- Electronic structure 28-34
  - and properties of rare-earth elements 35-8
- Element 61 16-20, 110
- Erbia, discovery of 5
- Europium, discovery of 11
- Gadolinium, discovery of 11
- Geochemistry of the rare-earth elements 43-51
- Hafnium, discovery of 15
- Heavy lanthanides 38-40
- Holmium, discovery of 10
- Illinium 16, 17
- Ionic radii of rare-earth elements 41-43
- Isotopicity of rare-earth elements 13, 101-7
- Lanthanide contraction 42
- Lanthanum, discovery of 5
- Light Lanthanides 38-40
- Lutetia, discovery of 11
- Lutetium 15
- Magnetic properties 54-6
- Mattauch's rule 19, 20
- Mechanical properties 54

- Mendeleev's periodic classification 7-9, 25-6, 33, 93
- Methods of separation of rare-earth elements 52ff
- Moseley and the prediction of the existence of an unknown element 15
- Neodymium, discovery of 11
- Neoytterbia, discovery of 11
- Neutron capture cross-sections in the rare earths 106
- Nuclear  
  chemistry of rare-earth elements 101-7  
  shell structure 107-9
- Occurrence of rare-earth elements 45
- Origin of the elements 111-4
- Paramagnetic properties of rare-earth elements 40
- Pauli principle, significance of 33-4
- Pearce's arrangement of rare-earth elements 95-6
- Periodic classification 7-9, 25-6, 33, 93
- Praeseodymium, discovery of 11
- Promethium 16-19, 110
- Properties of rare-earth elements 52ff
- Purification of rare-earth elements 62-72
- Samarium, discovery of 10
- Scattering of  $\alpha$  particles 26
- Spectroscopic analysis 7
- Spencer's arrangement of rare-earth elements 93, 94
- Terbia 6  
  discovery of 5
- Thulium, discovery of 10
- X-ray spectra 14, 19
- Ytterbite, occurrence of 2, 3
- Ytterbium, discovery of 10
- Yttria 2-5
- Yttrium group, electronic structure 37

